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ATC REPORT NO. ATC-9137

TREATABILITY STUDY REPORT

FOR

IN SITU LEAD IMMOBILIZATION

USING PHOSPHATE-BASED BINDERS

SITE LOCATION:
CAMP WITHYCOMBE, OREGON

PREPARED BY:
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Prepared for:
U.S. ARMY ENVIRONMENTAL COMMAND
ABERDEEN PROVING GROUND, MD 21010-5401

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REPLY TO
ATTENTION OF

TEDT-AT-SLE

19 May 2008

MEMORANDUM FOR Director, Environmental Security Technology Certification Program (Jeffrey Marqusee, Ph.D.), 901 North Stuart Street, Suite 303, Arlington, VA 22203

SUBJECT: Final Submittal of the Treatability Study Report for In-Situ Lead Immobilization Using Phosphate-Based Binders (ESTCP Project No. ER-0111) DTC Project No. 9-CO-160-000-572.

1. The US Army Aberdeen Test Center (ATC) is submitting the final subject report as approved.

2. The point of contact for this action is Mr. Gene L. Fabian. Mr. Fabian can be reached at (410) 278-7421 or by email at gene.fabian@us.army.mil.

FOR THE COMMANDER:

CHARLES D. VALZ
Director, Survivability/Lethality Directorate

Encl

EXECUTIVE SUMMARY

Metal contamination in soil is found on 69 percent of identified Department of Defense (DoD) sites with lead being the predominant heavy metal of concern. In situ solidification/stabilization methods are available that claim to reduce the environmental mobility of heavy metals by physically or chemically binding them in place. However, the metals remain in the soil in some form. The long-term fate of the remaining metals in the soil or chemical matrices they are bound within is unknown. Other issues that require investigation include the potential unintended or indirect environmental effects resulting from the in situ application of a chemical binding/treatment solution. Currently, these issues limit the use of in situ stabilization technologies.

The treatability study described in this report was designed to develop the information necessary to support the immobilization of lead contaminants in soil by in situ treatment with phosphate-based binders. The potential demonstration site for field treatment was a small arms firing range impact area at Camp Withycombe, Oregon. The study consisted of laboratory monitoring of samples treated to immobilize lead contamination using phosphate-based binders marketed by several vendors. The study was conducted by the U.S. Army Aberdeen Test Center (ATC) and Mississippi State University (MSU) under U.S. Army Developmental Test Command (DTC) Project No. 9-CO-160-000-572. This study was sponsored by the Environmental Security Technology Certification Program (ESTCP) under ESTCP Project No. ER-0111.

Technology performance was evaluated based on evidence of reduced soluble lead mobility, reduced human health risk, impact on soil biota, changes in soil physical properties, plant uptake, and mobility of other contaminants of concern associated with the proposed demonstration site. Data to support the evaluation of these criteria were produced through laboratory studies using soil collected at Camp Withycombe. The study utilized leaching and vegetation monitoring methods to evaluate the stability of the treated soil by attempting to build a body of evidence that indicated the formation of stable lead complexes.

The results of the study were mixed in that variability in lead stability was observed in soil treated by all vendors of in situ phosphate stabilization methods. The main results of the study were:

- TCLP analyses indicated a substantial reduction of lead mobility with most treated soil TCLP results below 5.0 mg/L. However, variations occurred in the samples as the treated soils aged during the 360-day monitoring period with lead TCLP results increasing and decreasing over time. In general, the data indicated a greater than 98.5 percent reduction in leachable lead in the soil. The SET results seemed to confirm this reduced mobility with a shift in lead concentrations from the more soluble fractions in the control soil to the less soluble fractions in the treated soils. However the variation in stability continues to call into question the long-term stability of the treated soils.

- Bioavailability reduction was evaluated through comparison between the untreated control and treated soil PBET results. The PBET lead concentrations in the treated samples indicated that a reduction in bioaccessible lead occurred when compared to the

control data. However, the treated soils exhibited significant variations in PBET lead concentrations during the monitoring period. In addition, at no time during the monitoring period was the bioaccessible lead exposure risk reduced to a level considered safe for residential or industrial use.

- Hyper-accumulating plant species were used in the lab study to identify general trends in plant bioavailability. The plant data indicated that the lead uptake can vary substantially according to the type of phosphate amendment. The lead uptake by plants can be expected to be influenced by a combination of the site-specific soil characteristics (i.e., mineral and organic constituents, biota, etc.), type of amendment(s) used, and the type and variety of local plants in the treated areas.

- All of the vendor-treated soils failed to meet the 0.75 mg/L TCLP UTS performance criteria with the exception of the Forrester 0-, 14-, 28-, 60-, and 120-day samples and the RMT 360-day sample. With the trends towards increasing TCLP lead concentrations observed in the data, a determination supporting long-term stability could not be made.

Field demonstration of the phosphate-based lead stabilization as an in situ treatment method was not recommended at Camp Withycombe for the following reasons:

- Human health risk reduction performance criteria were not met by any of the vendor amendments.

- Long-term stability of the lead in the soil was still questionable based on the data collected.

- The plant lead uptake study indicated a wide variability in lead availability. The variability was suspected to be the result of site-specific chemical and biological reactions, as well as plant species' metal uptake characteristics, that may limit the use of the technology for in situ applications.

ATC recommends that further research be conducted to investigate biogeochemical, microbial, and hydrological influences on the metals speciation and stabilization process. A better understanding of these factors is needed in order to predict the applicability and performance of phosphate amendments as a means of stabilizing metals on a site.

TABLE OF CONTENTS

APPENDIXES

LIST OF TABLES

LIST OF FIGURES

Page

ABBREVIATIONS

ACS	=	American Chemical Society
ANOVA	=	analysis of variance
ASTM	=	American Society of Testing and Materials
ATC	=	U.S. Army Aberdeen Test Center
bgs	=	below ground surface
CBD	=	Commerce Business Daily
CCA	=	chromated copper arsenate
CDC	=	Center for Disease Control
CEC	=	cation exchange capacity
CI	=	cone index
CL	=	confidence level
COC	=	contaminant of concern
DI	=	deionized
DoD	=	Department of Defense
DTC	=	U.S. Army Developmental Test Command
EC	=	effective concentration
ERDC	=	Engineer Research and Development Center
ESTCP	=	Environmental Security Technology Certification Program
FBI	=	Federal Bureau of Investigation
GLM	=	generalized linear model
HCl	=	hydrochloric acid
HDPE	=	high density polyethylene
HF	=	hydroflouric acid
IEUBK	=	Integrated Exposure Uptake Biokinetic
ISO	=	International Standards Organization
KD	=	known distance
MDL	=	method detection limit
MSU	=	Mississippi State University
MT^2	=	Metals Treatment Technologies
OAR	=	Oregon Administrative Rule
ODEQ	=	Oregon Department of Environmental Quality
ODOT	=	Oregon Department of Transportation
OMD	=	Oregon Military Department
PbB	=	blood lead level
PBET	=	Physiologically-Based Extraction Test
PRG	=	preliminary remediation goals
RH	=	relative humidity
SAB	=	Science Advisory Board
SD	=	short distance
SET	=	Sequential Extraction Test
SLV	=	screening level value
SOP	=	Standard Operating Procedure
SPLP	=	Synthetic Precipitation Leaching Procedure
TC	=	Total Carbon

TCLP = Toxicity Characteristic Leaching Procedure
TOC = Total Organic Carbon
TSS = Total suspended solid
UCS = unconfined compressive strength
USAEC = U.S. Army Environmental Center
USEPA = U.S. Environmental Protection Agency
UTS = Universal Treatment Standard
WES = Waterways Experiment Station

1.0 INTRODUCTION

1.1 Background

The purpose of the work described in this Treatability Study Report was to develop the information necessary to support the immobilization of lead contaminants in soil by in situ treatment with phosphate-based binders. The treatability study consisted of laboratory monitoring of samples treated to immobilize lead contamination using various phosphate-based binders. The treatability study was conducted by the U.S. Army Aberdeen Test Center (ATC) and Mississippi State University (MSU) under U.S. Army Developmental Test Command (DTC) Project No. 9-CO-160-000-572. This study was sponsored by the Environmental Security Technology Certification Program (ESTCP) under ESTCP Project No. ER-0111. Funding and support for this study was provided by the ESTCP and the U.S. Army Environmental Center (USAEC).

Heavy metal contamination of soils represents one of the largest remediation problems on military installations. Metal contamination in soil is found on 69 percent of identified Department of Defense (DoD) sites with lead being the predominant heavy metal of concern (United States Environmental Protection Agency (USEPA), 1997). Solidification/stabilization methods are currently the most used in situ metal-contamination treatment technologies. These methods reduce the environmental mobility or availability of heavy metals by physically or chemically binding them in place; however, the metals remain in the soil in some form. The long-term fate of the remaining metals or the soil or chemical matrices they are bound within is unknown. Other issues that require investigation include the potential unintended or indirect environmental effects resulting from the in situ application of a chemical binding/treatment solution. Currently, these issues limit the use of these in situ stabilization technologies.

This treatability study supports the potential conduct of a field demonstration of the in situ immobilization of lead in soil. The treatability study attempted to prove the immobilization of lead by building a body of evidence that indicates the formation of stable lead complexes. The future field demonstration will investigate stabilization performance and evaluate the effects that precipitation runoff and infiltration have on the in situ application of phosphate binders. The treatability study utilized treatment methods that employed various phosphate-based binders coupled with appropriate leaching and vegetation monitoring methods to evaluate the stability of the treated soil and the potential for metals transport.

1.2 Objectives of the Treatability Study

The main objective of this treatability study was to evaluate the performance of phosphate-based amendments that are marketed by several vendors. The results of the study were used to facilitate the selection of vendors for technology application in the field. Technology performance was evaluated based on evidence of reduced soluble lead mobility, reduced human health risk, impact on soil biota, changes in soil physical properties, plant uptake, and mobility of other contaminants of concern associated with the Camp Withycombe demonstration site in Oregon. Data to support the evaluation of these criteria were produced through laboratory studies using small arms firing range soil from the demonstration site at Camp Withycombe. The performance metrics for the objective are identified in section 3.

1.3 Test Site History/Characteristics

1.3.1 Project Site Location

Camp Withycombe is an Oregon National Guard facility located at 10101 Southeast Clackamas Road in Clackamas, Oregon. It is located just north of Highway 212 and east of its intersection with Interstate 205. The site is located in Clackamas County in Township 2 South, Range 2 East, Sections 9 and 10. The site covers approximately 235 acres. There are approximately 80 buildings on the property, most of which are located on the flat portion of the property to the south of Mount Talbert (Hart Crowser, Inc.).

Camp Withycombe was originally designated the Clackamas Firing Range. The camp was established by the U.S. Government in 1909, and the military began using the range that same year. The state constructed the first building on the site for the use by the National Guard in 1910. Over time, the camp was expanded from 93 acres to its present size, with the largest expansion-taking place in 1937 (Hart Crowser, Inc.).

The post served as a mobilization camp for cavalry and artillery for the Oregon National Guard until the end of World War I. During that time, it became the main supply depot for Soldiers in Oregon. After World War II, the 3670th Maintenance Company was organized on the post to repair heavy equipment. Heavy equipment maintenance is still the primary function of the facility today (Hart Crowser, Inc.).

1.3.2 Firing Range Description

The firing ranges are located in the central portion of the Camp Withycombe facility (Figure 1-1). The area behind the firing ranges (northeastern third of Camp Withycombe) consists of a wooded hillside (Hart Crowser, Inc.).

Three firing ranges are present at Camp Withycombe: Known Distance (KD), Federal Bureau of Investigation (FBI), and Short Distance (SD) (Figure 1-1). The KD and SD firing ranges include the following components: firing shed or firing line; pre-target area which is flat and grass covered; pre-target impact area where bullets falling short of the targets impact; target line; and a post-target impact area behind the target line. Only the post-target impact area of the FBI range remains. The KD range has been used since about 1909. The SD range was added around 1937. It is not known when the FBI range was first used (Hart Crowser, Inc.). Soil from the SD berm and the KD range impact area behind the targets will be used in the field demonstration. During the 1950s, the firing ranges were used by the Oregon National Guard, National Rifle Association teams, the FBI, Treasury Department, and state and local police agencies. Live firing ceased in 1995 and is no longer conducted on these ranges (Hart Crowser, Inc.).

The federal government deeded the land to the state of Oregon in 1956. Recently, portions of the camp were transferred from the Oregon Military Department to the Oregon Department of Transportation (ODOT). The ownership transfer occurred in conjunction with the ODOT Sunrise Corridor Project. The area north of the southern right-of-way line of the new freeway was included in the property transfer (Hart Crowser, Inc.).

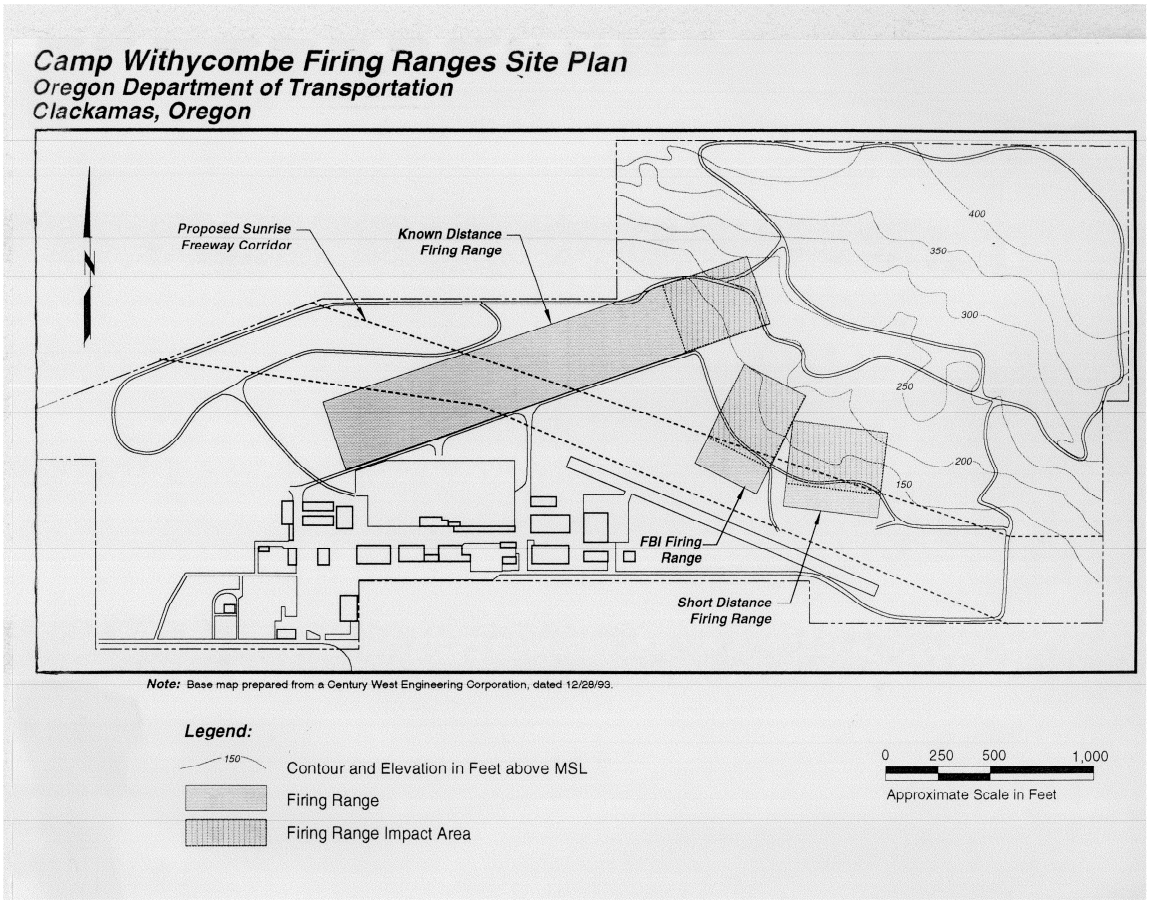


Figure 1-1. Camp Withycombe range overview (Hart Crowser, Inc.).

The impact areas are the major concern with respect to lead contamination. The respective widths of these areas are roughly equal to the width of each firing range (KD, 400 ft; FBI, 300 ft; SD, 600 ft). The KD range and FBI range post-target impact areas are in the hillside behind the ranges. The SD range post-target impact area is primarily a berm behind the target line; however, stray rounds and rounds that skip over the berm impact the hillside behind the berm (Hart Crowser, Inc.).

1.3.3 Previous Investigations at the Camp Withycombe Ranges

The following site investigations (Hart Crowser, Inc.) have been conducted at the Camp Withycombe firing ranges:

Limited Site Investigation
Camp Withycombe
Dames & Moore
Prepared for Oregon Department of Transportation
July 12, 1991

Remedial Action Plan
Camp Withycombe Firing Ranges
Century West Engineering Corporation
Prepared for Oregon Department of Transportation
January 31, 1994

Site Investigation
Camp Withycombe Firing Ranges
Hart Crowser, Inc.
Prepared for Oregon Department of Transportation
August 30, 1995

Firing Range Treatability Study
Camp Withycombe
Clackamas, Oregon
Hart Crowser, Inc.
Prepared for Oregon Department of Transportation
November 17, 1995

Additional Site Characterization
Camp Withycombe Firing Ranges
Clackamas, Oregon
Hart Crowser, Inc.
Prepared for Oregon Department of Transportation
June 28, 1996

The previous investigations included soil sampling from the firing ranges as well as surface and subsurface water sampling. Soil sampling has included surface soil sampling and soil cores down to a maximum depth of 3.5 ft-bgs with the majority of the cores being taken between 0 and 2 ft-bgs. The overall soil pH ranged from 6.2 to 7.8. The soil sampling for total priority pollutant metals (USEPA Methods 6010B/6020/7471) detected concentrations above background for antimony, arsenic, chromium, copper, lead, nickel, silver, and zinc. Of these, only arsenic and lead, at concentrations up to 150 mg/kg and 95,000 mg/kg, respectively, exceeded the Oregon Department of Environmental Quality (ODEQ) maximum allowable soil

concentration. The highest lead levels were found in the range impact areas within the 0 to 2 ft-bgs depth with the surface soils (0 to 6 in.) having the highest concentrations. Leachable lead levels, as determined using the Toxicity Characteristic Leaching Procedure (TCLP) (USEPA Methods 1311/6020), were detected at concentrations up to 920 mg/L in the impact area samples (Hart Crowser, Inc.).

Analyzed groundwater samples had lead concentrations ranging from 0.065 to 0.600 mg/L. No dissolved lead was detected. Total suspended solid (TSS) concentrations in the groundwater ranged from 1,000 to 71,000 mg/L. The lead present in the groundwater is associated with the suspended solids. It is unlikely that water percolating through unsaturated soil to groundwater will leach significant concentrations of lead due to the local soil pH values (6.2 to 7.8). The concentration of lead in the groundwater likely represents background concentrations (Hart Crowser, Inc.).

Stationary water present at the base of the post-target area of the KD range was sampled for surface water concentrations. Surface water samples were analyzed for total and dissolved lead and total suspended solids. Total lead ranged from 0.004 to 1.67 mg/L. Dissolved lead ranged from <0.002 (nondetect) to 0.013 mg/L. The sample with the highest total lead also contained the highest total suspended solids (637 mg/L) (Hart Crowser, Inc.).

Based on the sampling results, Century West estimated the amount of soil with lead contamination greater than 2,000 mg/kg on each range as shown in Table 1-1 (Hart Crowser, Inc.).

TABLE 1-1. ESTIMATED SOIL VOLUMES REQUIRING CLEANUP
(Hart Crowser, Inc.)

KD Range	4,300 cubic yards
FBI Range	1,600 cubic yards
SD Range	5,525 cubic yards
Total	**11,425 cubic yards**

FBI = Federal Bureau of Investigation.
KD = Known Distance.
SD = Short Distance.

2.0 TECHNOLOGY DESCRIPTION

2.1 Technology Development and Application

Several technologies have been used in the remediation of heavy-metal contamination in soils. Many remediation technologies have proven to be costly, short-lived, or lacking aesthetics. Examples of commonly employed remediation technologies include extraction, soil washing, chemical or physical treatment, excavation of contaminated material, and fencing to limit access (Rabinowitz; Cotter-Howells and Caporn). Phosphate-based remediation of heavy metals is an emerging technology that promises to address the need to cost-effectively remediate metals in soils. The fundamental geochemistry of the technology is well described in the technical literature and reviewed in this section.

The technology described herein exploits the relative insolubility of lead phosphates in soil systems. Considerable evidence exists in the literature supporting the assertion that lead phosphates are among the most stable forms of lead found under environmental conditions. Furthermore, this evidence suggests that lead phosphates form rapidly when sufficient phosphate is present (Ruby, et al, 1994). Several authors have suggested that apatite [$Ca_5(PO_4)_3OH$] effectively immobilizes lead in soil solutions by sequestering the lead to form hydroxypyromorphite [$Pb_5(PO_4)_3OH$] (Rabinowitz; Cotter-Howells and Caporn). In addition, a thorough review of the current literature was conducted as part of this study. The results of this literature review are included for reference in Appendix A.

The relative solubility products (K_{sp}) of a number of lead minerals are presented in Table 2-1. These data demonstrate that lead phosphates are significantly less soluble than oxides, hydroxides, carbonates, and sulfates of lead under equilibrium conditions. The solubility products (Table 2-1) for the pyromorphite minerals [$Pb_5(PO_4)_3X$], where X is either a halide or hydroxide, consisting of chloro-, bromo-, hydroxy-, and fluoropyromorphite, are $10^{-84.4}$, $10^{-78.1}$, $10^{-76.8}$, and $10^{-71.6}$, respectively.

TABLE 2-1. THEORETICAL SOLUBILITY OF SOME LEAD MINERAL PHASES[a]

Lead Phase	Chemical Composition	Log K_{sp}
Litharge	PbO	12.9
Anglesite	$PbSO_4$	-7.7
Cerussite	$PbCO_3$	-12.8
Galena	PbS	-27.5
Chloropyromorphite	$Pb_5(PO_4)_3Cl$	-84.4
Hydroxypyromorphite	$Pb_5(PO_4)_3OH$	-76.8
Fluoropyromorphite	$Pb_5(PO_4)_3F$	-71.6
Bromopyromorphite	$Pb_5(PO_4)_3Br$	-78.1
Corkite	$PbFe_3(PO_4)(SO_4)(OH)_6$	-112.6
Hinsdalite	$PbAl_3(PO_4)_2(SO_4)(OH)_6$	-99.1
Plumbogummite	$PbAl_3(PO_4)_2(OH)_5 \cdot H_2O$	-99.3

[a]Modified from Ruby et al, 1994.

These solubility product data indicate a thermodynamic stability sequence for the lead pyromorphite minerals as follows; $Pb_5(PO_4)_3Cl > Pb_5(PO_4)_3Br > Pb_5(PO_4)_3OH > Pb_5(PO_4)_3F$. In contrast, the solubility products for anglesite ($PbSO_4$), cerussite ($PbCO_3$), galena (PbS) and litharge (PbO) are $10^{-7.7}$, $10^{-12.8}$, $10^{-27.5}$, and $10^{12.9}$, respectively. Ruby and co-workers, have stated that these data demonstrate that lead pyromorphite minerals have significantly lower aqueous solubilities than commonly found lead ore materials (galena, anglesite, and cerussite), lead in paint pigments (lead carbonate as $PbCO_3$), as well as lead minerals commonly found in association with internal combustion engines (anglesite and cerussite). Pyromorphites have been associated with the stabilization of lead compounds in mine-tailings and reportedly have been found in highly contaminated garden soils. It is believed that the presence of pyromorphites in these cases has limited the bioavailability of lead found in the associated soils (Rabinowitz).

Several lead-phosphate complexes may occur in soils. Chloropyromorphite ($Pb_5(PO_4)_3Cl$) is the most insoluble (Log K_{sp} = -84.4) of the pyromorphite minerals. Alloway has stated that chloropyromorphite may control the solubility of environmentally occurring lead throughout a wide range of soil pH values. This is especially true in soils with high phosphorus content, such as sewage sludge amended soils.

Phosphate binders can be added in many forms that will form the desired pyromorphites; however, the kinetics of the reaction depends on the phosphate species. This may be due to the ability of the specific binder to mix efficiently in the contaminated soil or due to the reactive nature of the specific species of phosphate applied to the site. In situ treatment methods include land-farming application of the binder (plowing and grading), injection, and surface application of the binder, as well as mixing the binder with the soil in situ via auguring. Each vendor that successfully treated the soil samples provided during the laboratory treatability study had the opportunity to propose their specific phosphate species and application method. These proposals, along with the laboratory treatability results, were used to select the vendors that may be utilized in future field demonstrations.

2.2 Factors Affecting Cost and Performance

A number of factors may influence the performance of the technology. These factors include application system design and operation and physical/chemical characteristics of the treatment site. Design factors include site characterization to a level of detail that allows adequate reagent application. Operational factors include those factors that influence the application of reagents (e.g., pressures and rates of reagent application as well as mixing depth). Additionally, post-application monitoring must be performed. The physical and chemical characteristics of the site may affect the success of the technology. The effectiveness of the treatment is expected to be dependent on the soils at the site. Chemical factors to consider include soil pH and the presence of co-contaminants. Physical factors of consideration include the presence of groundwater, the topography of the site (e.g., surface runoff), and the permeability of the soil.

In situ treatment of lead contaminated sites offers potential cost savings over existing technologies. The reagents used to form lead-phosphate complexes may be easily applied. Depending upon the site characteristics, topical application of a liquid or slurry may be all that is required. Other in situ application methods include topical application followed by rototilling, plowing, or auguring for a homogeneous application in the soil matrix.

2.3 Advantages and Limitations of the Technology

To date, the phosphate binding of lead when coupled with solidification has been successfully used only for soils and sediments targeted for landfill disposal. In situ treatment of lead contaminated sites offers several potential advantages over those existing technologies in use. Depending upon the site characteristics, application methods may consist of simply topically applying a liquid or slurry, or topical application followed by rototilling, plowing, or auguring for a homogeneous application in the soil matrix. The potential ease of application may allow the treatment of lead-contaminated soils at costs ranging from $7 to $40 per ton of material treated. Current costs for the conventional treatment of lead contaminated sites range from $137 to $237 per ton of material treated. Clearly, ease of treatment and the low costs of treatment are the major advantages of the technology. Additionally, the use of phosphate-binders to treat lead may also effectively immobilize other heavy metals that may be contaminants of concern. The metals that may be stabilized by this treatment include lead, zinc, copper, cadmium, nickel, uranium, barium, cesium, strontium, plutonium, thorium, and other lanthanide and actinide metals.

There are several limitations to the use of phosphate binders for the in situ treatment of heavy metal contaminated soils and sediments. Some of these limitations are similar to those presented for the solidification/stabilization of metal contaminated soils and include;

- The volume of the treated material may increase with the addition of the binding agents and any required reagents.

- Organic contaminants, in general, are not effectively treated using phosphate-based binding agents.

- Volatilization and emission of volatile organic compounds that may be present at the site may occur during the mixing process.

The use of phosphate-based binders is a relatively new technology and long-term studies are lacking. This lack of long-term studies combined with the fact that the reagents used in the phosphate-based binding process vary with the vendor applying the technology has left a void in the understanding of the fate and environmental impact of the reagents used, as well as non-target species. Also, the fate of lead-phosphate complexes when lead-phosphate enters the digestive tract needs to be investigated.

3.0 TREATABILITY STUDY DESIGN

3.1 Performance Objective

The objective of this treatability study was to evaluate technology performance prior to selection of vendors for technology application in the field. Technology performance was evaluated based upon evidence of reduced soluble lead mobility, reduced human health risk, impact on soil toxicity, changes in soil physical properties, plant uptake, and mobility of other contaminants of concern associated with the Camp Withycombe demonstration site. Each of these performance criteria was considered a subset of the objective. As such, performance criteria were specified for each subordinate objective. The weight of each subordinate objective was not the same. Subordinate objectives of lesser importance in the overall evaluation of the technology were noted as secondary. Table 3-1 summarizes the subordinate objectives, performance metrics and relative importance to the evaluation of the main objective.

3.1.1 Performance Criteria

The objective of this treatability study was to evaluate the ability of several commercially available phosphate-based metal treatment technologies to immobilize and stabilize lead through an in situ technology application. Regulatory acceptance of the technology was to be based upon the immobilization of the contaminants and the reduced risk posed by the contaminants contained in the site soil. Subordinate objectives are as follows:

1) Evaluate soluble lead mobility reduction.

2) Evaluate ease of use.

3) Evaluate human health risk reduction.

4) Evaluate mobility impact to other existing metal contaminants.

6) Evaluate impact of technology on soil toxicity.

7) Evaluate impact of amendments on soil properties.

8) Evaluate the reduction in lead bioavailability using metal hypo-accumulating plants as indicators.

9) Evaluate ability to meet regulatory clean-up standards for land disposal and storm water runoff.

A discussion of how each subordinate objective pertains to the overall objective of the treatability study and how the identified data was used to address the subordinate objectives follows in section 3.1.2.

TABLE 3-1. PERFORMANCE OBJECTIVES

Type of Performance Objective	Primary Performance Criteria	Expected Performance (Metric)	Laboratory Treatability Study Derived Data	Primary or Secondary
Qualitative	1. Reduce soluble lead mobility.	Evidence of insoluble lead phosphate species formation (TCLP, SPLP, and SET results).	TCLP, SPLP, and SET	Primary
	2. Ease of use.	Method of amendment application, projected cost, and time required to treat the site.	Proposal review	Secondary
Quantitative	3. Reduce human health risks.	Reduce bioavailability to acceptable levels. (Site-specific reduction to be determined based on current bioavailability and lead concentration.)	PBET	Primary
	4. Evaluate mobility of other metal contaminants present at the site.	Arsenic TCLP less than 5 mg/L[a]. Antimony TCLP less than 1.15 mg/L. Copper TCLP less than 100 mg/L.	TCLP	Primary
	5. Evaluate the impact of the technology on soil toxicity.	Changes in soil toxicity from the control.	MICROTOX®	Secondary
	6. Evaluate amendment effects on the physical properties of the soil.	Changes in permeability, UCS, volume, and particle size distribution from the control.	Permeability, UCS, Bulking, and Particle Size Distribution.	Secondary
	7. Evaluate the reduction in lead bioavailability using metal hypo-accumulating plants as an indicator.	Changes in plant lead uptake in vegetation between treated soil and control.	Lead concentration in plant stems, and leaves.	Secondary
	8. Meet regulatory standards.	Lead TCLP less than 0.75 mg/L UTS. ODEQ acceptance.	TCLP	Primary

[a]The arsenic leachate level of 5 mg/L is a threshold level. Failure to obtain this level will eliminate the technology from further consideration for on-site disposal. An objective level of 4 µg/L has been added. This is the desired level for in situ site cleanup.

ODEQ = Oregon Department of Environmental Quality.
PBET = Physiologically-Based Extraction Test.
SPLP = Synthetic Precipitation Leaching Procedure.
SET = Sequential Extraction Test.
TLCP = Toxicity Characteristic Leaching Procedure.
UCS = Unconfined compressive strength.
UTS = Universal Treatment Standard.

3.1.2 Data Analysis, Interpretation, and Evaluation

Several phosphate-based metal treatment technologies are being marketed to immobilize and stabilize lead contaminated soil in situ. MSU provided representative samples of Camp Withycombe range soil to vendors marketing these technologies for treatment with their respective phosphate-based amendments. These treated samples were used by MSU in laboratory treatability studies to address the objectives identified in Table 3-1. The vendors were evaluated based on the treatability study performance metrics and the review of a proposal solicited from each vendor for conducting the proposed field demonstration. The primary performance metrics were focused on evaluating the ability of the lead-phosphate complex to meet leachate (Toxicity Characteristic Leaching Procedure (TCLP)) criteria and the stability of the lead-phosphate complex. Long-term stability, or stable complex formation, was investigated through the use of the Sequential Extraction Test (SET). The SET permitted the inference of whether or not the insoluble pyromorphite compound had formed. Additional primary performance metrics included an evaluation of mobility of other metal contaminants at the site and an evaluation of the reduction of human health risk to the stabilized lead complex. Failure to reach specified metal or phosphate leachate requirements, develop evidence of long-term stability, or to reduce bioavailability to humans resulted in the vendor processes being eliminated from consideration for participation in the field demonstration. In order to be selected for participation in the field demonstration, all primary objective performance metrics must have been met (Table 3-1).

The performance metric of each subordinate objective is discussed in the following paragraphs. In certain cases, defined standards or target levels were not established. In these cases, consultation with the ODEQ was conducted to discuss the acceptability of the achieved stabilization for future use on the demonstration site.

3.1.2.1 Evaluate Soluble Lead Mobility Reduction

Determining lead solubility reduction was a primary performance metric. The stabilization technology is designed to form relatively insoluble lead complexes in the soil matrix. In order to evaluate if the lead was in an insoluble form, a series of leaching tests was conducted (TCLP, Synthetic Precipitation Leaching Procedure (SPLP), and SET). Although these tests do not definitively determine whether a pyromorphite compound had been formed, the results were indicative of insoluble complex formation. A concern associated with the use of leaching tests was that the extraction process may catalyze the reaction between the metals and the phosphate amendment, thus enabling the process to produce the insoluble compound. It was for this reason that the series of leaching tests were performed. The TCLP determined the pre- and post-treatment regulatory waste characteristics of the soil, even though the acid extraction process used to prepare the TCLP samples likely drove the formation of the insoluble complexes. The SPLP evaluated the potential for lead leaching under the influence of acidic precipitation. The results of this were indicative of the natural solubility of lead under normal weathering conditions in the field as opposed to the harsher conditions that may be experienced in a co-disposal landfill which was the scenario that the TCLP was designed to simulate. The SET series of extractions helped evaluate the physicochemical condition of the lead in the untreated control and treated soil. This series of progressively stronger extractions indicated the conditions

under which the lead was leachable, if at all, and permitted the inference of whether or not insoluble pyromorphite compounds had been formed based on the extract fractions in which the lead was found to leach.

This quantitative data permitted a subjective evaluation of the degree of stabilization. The data allowed the inference of whether the formation of insoluble complexes had occurred that support the potential for long-term stability of the lead. A direct comparison between an untreated control and treated soil results was performed to evaluate solubility reduction. Also, comparison to regulatory waste characteristic contaminant levels was made to gauge the effectiveness of the stabilization.

3.1.2.2 Evaluate Ease of Use

Ease of use was a secondary objective that was evaluated based upon the review of the proposals submitted by the vendors for the conduct of the field demonstration. The viability of the vendors' proposed application methods were subjectively evaluated based upon the demonstration site characteristics. The other factors of projected costs and time required to treat the site were evaluated for viability and a comparison between the vendors' proposals was performed.

3.1.2.3 Evaluate Human Health Risk Reduction

Determining health risk reduction was a primary performance metric. This determination was made based on the measured reduction of the bioaccessibility of lead. The bioavailability of the lead in the untreated control and treated soil was measured using the Physically Based Extraction Test (PBET) which is a laboratory extraction test designed to simulate the digestive tract of humans. The bioavailability reduction was evaluated through comparison between the untreated control and treated soil PBET results.

The data developed was used not only to provide a measure of bioavailability reduction, but also to estimate the risk associated with the stabilized lead that is left in the soil. The biological absorption data produced by the PBET were input into the Integrated Exposure Uptake Biokinetic (IEUBK) Model to estimate the risk associated with the concentration of stabilized lead in the soil (USEPA, 2001). The performance metric was based on whether or not the stabilization process had been able to reduce the human lead uptake risk to the point that the treated soils could be left on-site. The risk reduction of the treated metals was discussed with ODEQ to evaluate its impact on proposed site cleanup criteria and on the viability of use of the technology at the demonstration site.

3.1.2.4 Evaluate Mobility Impact to Other Existing Metal Contaminants

Determining the mobility of the arsenic, copper, and antimony found in the soil was a primary performance objective. Additional metals were included in the mobility analysis dependent upon the outcome of the baseline metals characterization results. Comparison between the untreated control and treated soil TCLP results were made to determine the effects of the stabilization amendments on the mobility of these metals. The mobility of the treated

metals was discussed with ODEQ to evaluate their impact on proposed site cleanup criteria and on the viability of use of the technology at the demonstration site. A defined cleanup standard for in situ stabilization of arsenic, copper, and antimony had not been established by regulatory agencies. Unless otherwise determined by ODEQ, the stabilization amendments that failed to meet the TCLP leachate thresholds of 5 mg/L, 100 mg/L, and 1.15 mg/L for arsenic, copper, and antimony, respectively, were not selected to proceed to the field demonstration. The arsenic leachate level of 5 mg/L was a threshold level only. A conservative objective level of 4 µg/L had also been established for the TCLP extract. This was the desired level for in situ site cleanup based on Oregon Administrative Rule (OAR) 340-122-045, reference Leachate Concentration in Appendix 1 of the Numerical Soil Cleanup Levels.

Although not specified as a performance criterion, the mobility of the phosphate placed in the amended soils was also characterized. Regulatory limits for phosphate in storm water runoff or groundwater are typically site specific. Non-point source discharge limits may be established to prevent eutrophication of aquatic ecosystems. Discharge limits for phosphate have not been investigated for the Camp Withycombe site. The control and treated samples were characterized for leachate phosphate concentrations resulting from deionized (DI) water leaches of the soil. This data was discussed with ODEQ to evaluate its impact on possible non-point source discharge levels and the viability of use of the technology at the demonstration site.

3.1.2.5 Evaluate Impact of Technology on Soil Toxicity

Determining the technology's impact on toxicity was a secondary performance objective. Comparison between the untreated control and treated soil MICROTOX® results was made to evaluate whether any changes had occurred in the soil toxicity as a result of the application of the stabilization amendments. Any change in toxicity was discussed with ODEQ to evaluate its impact on the viability of use of the technology at the demonstration site.

3.1.2.6 Evaluate Impact of Applying Amendments upon Soil Properties

Determining the technology's impact on the soil's geophysical properties was a secondary performance objective. Comparison between the untreated control and treated soil permeability, unconfined compressive strength (UCS), bulking, and particle size distribution results were made to evaluate whether any soil physical property changes have occurred as a result of the application of the stabilization amendments. Any soil physical property changes were discussed with the ODEQ and the ODOT to evaluate their impact on the viability of use of the technology at the demonstration site.

3.1.2.7 Evaluate the Reduction to Lead Bioavailability Using Plants

Evaluating the phosphate treatment technology's impact on the plant bioavailability of lead was a secondary performance objective. A comparison between the untreated control and treated soil using a hypo-accumulator plant species was made to evaluate whether any change in the plant metal uptake had occurred as a result of the application of the stabilization amendments. Any changes in lead uptake by plants or obvious affect on plant health were discussed with ODEQ and ODOT to evaluate its impact on the viability of use of the technology at the demonstration site.

3.1.2.8 Evaluate Ability to Meet Regulatory Cleanup Standards for Land Disposal

Determining the technology's ability to meet regulatory cleanup standards was a primary performance objective. A defined cleanup standard for in situ stabilization of lead had not been established by regulatory agencies. As a result, the cleanup standard for off-site land disposal of lead contaminated soil was selected to gauge the success of the in situ lead stabilization process. The USEPA land disposal standard is a lead TCLP result of 0.75 mg/L. Comparison of the treated soil TCLP results to this standard was made. The TCLP results for lead, as well as any other contaminants of concern, were discussed with ODEQ to evaluate their impact on the use of the technology at the demonstration site. Unless otherwise determined by ODEQ, technology that failed to meet the land disposal standard was not elected to proceed to the field demonstration.

3.1.3 Performance Confirmation Methods

An experimental design was selected to enable the evaluation of the technology in a controlled laboratory setting using actual range soils. This was done to minimize variables and expedite a feasibility evaluation of the technologies. The effect of executing this experimental design was to reduce the size and expense of the proposed field demonstration phase.

A flowchart depicting the conduct of the treatability study is provided in Figure 3-1. In the depicted approach, the vendors selected to participate in the treatability study were provided with up to a 5-gallon sample of soil and Camp Withycombe demonstration site information which they used to develop the specific amendment mix and application methods for treatment of the site soil. Each vendor then treated a 5-gallon sample of soil at MSU for use in the treatability study. Each vendor also submitted a proposal for treating the soil at the Camp Withycombe demonstration site that included a description of the amendments and application methods, time for treatment, and a breakdown of demonstration and projected treatment costs for the entire site.

The treated samples and the untreated control were monitored for a period of 360 days. This extended period of monitoring under controlled conditions was selected to gather data to address concerns resulting from observations of other studies done by IT Corp and USEPA in which lead mobility was observed after stabilization. The results of these other studies have not been published. Lead mobility concerns were identified through telephone conversations between R. Mark Bricka, Ph.D. and the principle investigators of those studies. The verbal concerns that had arisen from these conversations warranted the long period of observation in the laboratory to attempt to identify if the lead mobility increases over time.

After treatment of the 5-gallon soil samples at MSU, MSU initiated the 360-day treatability study and conducted a greenhouse study to evaluate the reduction in plant lead bioavailability from the treated soil. The sample and plant study results were evaluated based on the guidance provided for each subordinate objective as described in section 3.1.2.

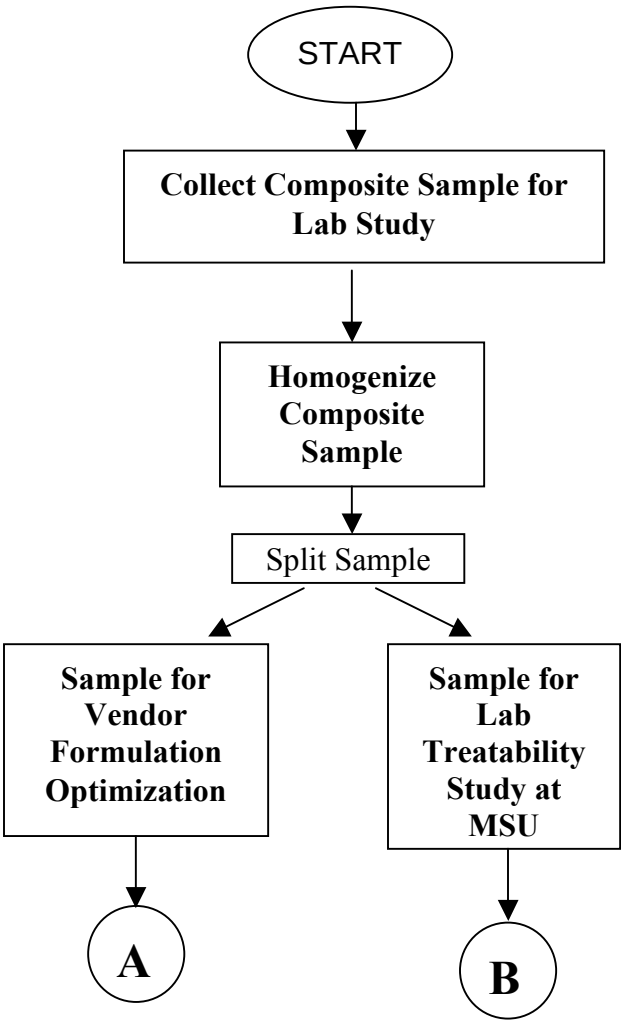


Figure 3-1. Treatability study approach flowchart.

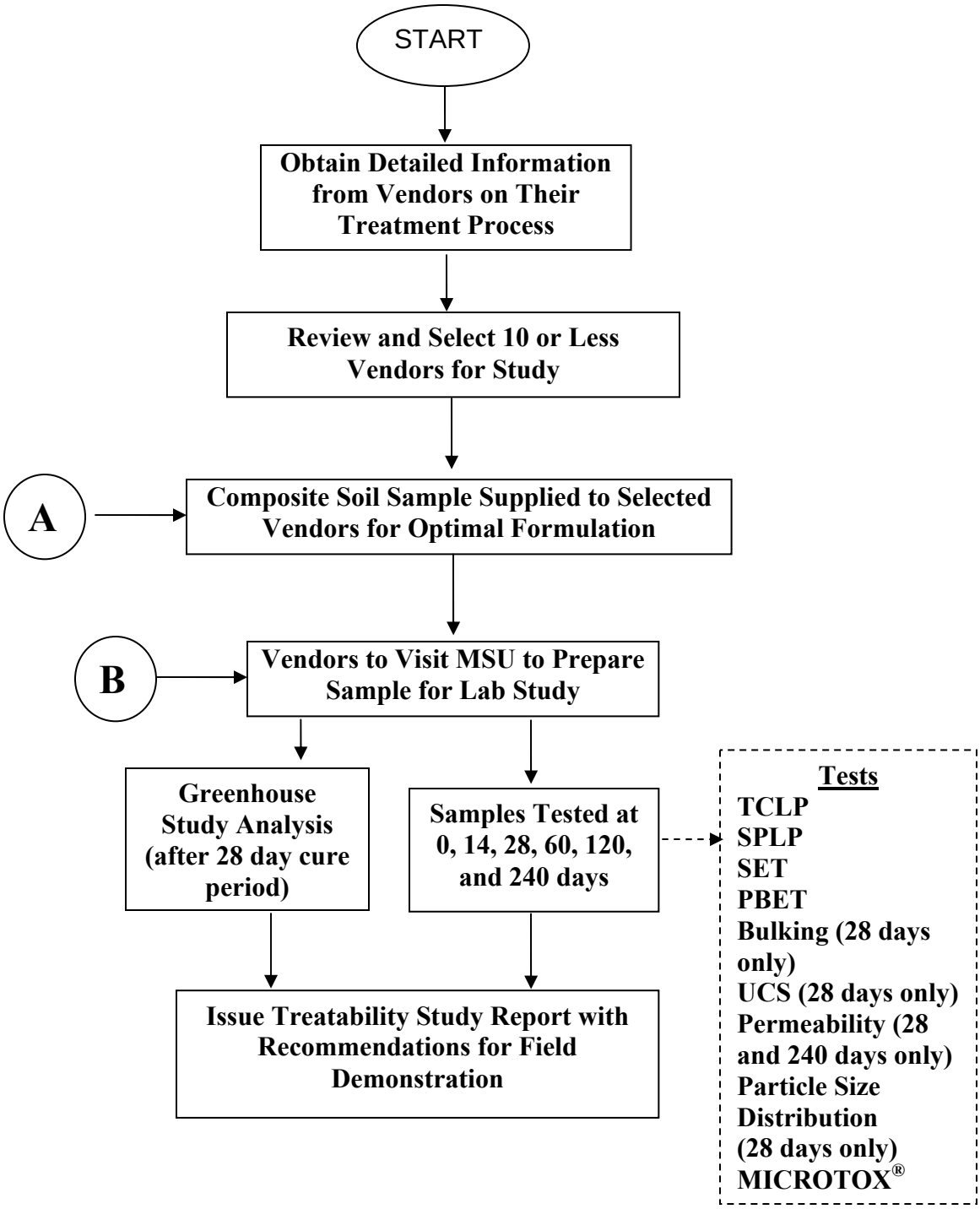


Figure 3-1 (Cont'd)

3.2 Pre-Treatability Study Activities

Prior to conducting the treatability study, information was solicited from available vendors, and soil was collected from the proposed Camp Withycombe demonstration site for use in the treatability study. The vendor selection phase was initiated by the placement of a Commerce Business Daily (CBD) announcement soliciting potential vendors to participate in the technology treatability study. In addition, a web and patent search identified candidate vendors of phosphate-based technologies suitable for immobilization of lead in small-arms ranges. These vendors were contacted directly and requested to participate in the technology treatability study. Table 3-2 identifies the vendors that expressed an interest in participating.

The vendors identified in Table 3-2 were then requested to submit information packets. The information requested included specific information on the vendor's technology and application methodology, performance history with the technology, support requirements, waste generation and handling methods, scientific background pertaining to technology development and use, general company history, and specific laboratory and field demonstration requirements. Six vendors responded with the requested information.

The vendor packets were reviewed by the members of the Science Advisory Board (SAB) identified in Table 3-3. This board, composed of subject matter experts, scored the vendor packets and selected five candidate vendors for participation in the laboratory treatability study. The five vendors selected were Shaw International, Metals Treatment Technologies, Sevenson Environmental Services, Forrester Environmental Services, and RMT. With the exception of Sevenson Environmental Services, these vendors participated in the lab study.

TABLE 3-2. INITIAL LIST OF CANDIDATE VENDORS

Company	POC	Address
Forrester Environmental Services	Keith Forrester	78 Tracy Way Meredith, NH 03253 (603) 279-3407
ARS Technologies	John Haselow	271 Cleveland Avenue Highland Park, NJ 08904 (732) 296-6620
RMT	Jim Crowley	P.O. Box 8923 Madison, WI 53708-8923 (608) 831-4444
SEMS Inc.	Brian Smith	11628 South Choctaw Drive Baton Rouge, LA 70815 (225) 924-2002
Sevenson Environmental Services	Charles McPheeters	8270 Whitcomb Street Merriville, IN 46410 (219) 756-4686
Hanford Nuclear Services	Dr. R. Soudarajan	28 Court Square West Plains, MO 65775 (417) 257-2741
MFG	Judith Bolis	4900 Pearl East Circle Suite 300W Boulder, CO 80301 (303) 447-1823
AWS Remediation	Joseph Santa	One Triangle Lane Export, PA 15632 (724) 733-1009
EnviroData Group	Stewart North	Director of Business Development EnviroData Group, LLC 2520 Regency Road Lexington, KY 40503 Office (859) 276-3506 Fax (859) 278-5665 New Cell (859) 338-0637 snorth@envirodatagroup.com
Apollo Environmental Strategies	Tina Moore	222 N. Story Road Suite 130 Irving, TX 75061 (972) 313-7866
Metals Treatment Technologies	James Barthel	12441 W. 49th Avenue Suite 3 Wheat Ridge, CO 80033 (303) 456-6977

TABLE 3-2 (CONT'D)

Company	POC	Address
Remedius	Thomas J. De Grood	2810 Duniven Circle Suite 102 Amarillo, TX 79109
Shaw International	Ernest Stine	304 Directors Drive Knoxville, TN 37923-4700 (865) 694-7347
Westinghouse - Savannah River	Miles Denham	Building 773-42A, Room 218 Aiken, SC 29808 (803) 725-5521

TABLE 3-3. SCIENCE ADVISORY BOARD MEMBERS

Member	Affiliation	Contact Information
R. Mark Bricka, Ph.D.	Mississippi State University	(662) 325-1615 (voice) (662) 325-2482 (fax) bricka@che.msstate.edu
Mr. Gene L. Fabian	U.S. Army Aberdeen Test Center Military Environmental Technology Demonstration Center Aberdeen Proving Ground, MD	(410) 278-7421 (voice) (410) 278-1589 (fax) Gene.Fabian@atc.army.mil
Mr. Mike Channell	U.S. Army Corps of Engineers - ERDC Vicksburg, MS	(601) 634-2386 (voice) (601) 634-8283 (fax) ChannellM@wes.army.mil
Mark Zappi, Ph.D.	Mississippi State University	(662) 325-7203 (voice) (662) 325-2482 (fax) zappi@che.msstate.edu
Steve Larson, Ph.D.	U.S. Army Corps of Engineers - ERDC Vicksburg, MS	(601) 634-3431 (voice) (601) 634-2742 (fax) LarsonS@wes.army.mil

ERDC = Engineer Research and Development Center.

4.0 MATERIALS AND METHODS

4.1 Treatability Study Sample Collection

To support the treatability study, MSU collected a 55-gallon composite soil sample from both the SD and KD range impact areas at Camp Withycombe for a total soil sample volume of 110 gallons in accordance with an approved sample plan (ATC). This sample was collected in August 2002. At MSU, the soil was homogenized and subdivided into 5-gallon samples for distribution to vendors and to support laboratory treatability studies. Before homogenization, the soil was passed through a 9.5 mm sieve to remove large particles and organic matter. Initially, the 55 gallons of soil collected from the KD range were homogenized separately from the 55 gallons of soil collected from the SD ranges. The homogenization procedure consisted of mixing two 5-gallon buckets of soil at one time. The mixture from the two buckets was then put into a concrete mixer and stirred for 10 to 15 minutes to attempt to thoroughly homogenize the soil. After mixing, the soil was poured into a splitter for an unbiased separation of the soil. Approximately 1/2 gallon of soil from each bucket was cascaded into 11 new 5-gallon buckets. This procedure was repeated for all 11 original buckets of soil. Then the 11 new buckets of soil was cascaded back into the original 11 buckets using the same procedure. This provided a homogenized soil sample for the KD range and the SD range. These soils were analyzed to verify satisfactory homogenization. After analysis the soil was homogenized again. For this homogenization, soil from the KD range was mixed with the soil from the SD ranges. The same cascading procedure as described above was performed on all 22 5-gallon buckets of the soil, with the exception that a splitter was not used. The end result was a 110-gallon homogenized soil sample that would be representative of the soils to be tested during the future pilot scale demonstrations on site.

4.2 Baseline Soil Characterization

4.2.1 Homogenization Assessment

Upon completion of the homogenization of the composite soil sample, samples were collected from each 5-gallon bucket of soil to determine the success of the homogenization activities. Three samples were collected from each of the 22 5-gallon buckets of soil. These samples were collected from the top, middle, and bottom of each bucket. The samples were digested (USEPA Method 3051) and analyzed for total lead using USEPA Method 6010B. Total lead was selected as the indicator for homogenization success since it is the most predominant contaminant introduced at the site. The results of the homogenization lead analyses are shown in Figure 4-1. The average lead concentration was determined to be 14,213.0 mg/kg with a median concentration of 12,394.9 mg/kg and a standard deviation of 5,730.5 mg/kg. These samples were also analyzed for arsenic using USEPA Method 7010. The results of the arsenic analyses are shown in Figure 4-2. The average arsenic concentration was determined to be 16.66 mg/kg with a median concentration of 15.49 mg/kg and a standard deviation of 4.50 mg/kg. Although there are significant variations in the lead concentrations throughout the sample buckets, this degree of homogenization is considered to be acceptable to the principle investigators, based on previous experience. These variations are typical of the heterogeneous nature of the metal contaminants in the environment. Significant variations are expected within each 5-gallon bucket of soil and constitute a treatment variable that must be addressed by the vendors when developing their treatment process.

4.2.2 Soil Characterization

As outlined in Figure 3-1 both chemical and physical testing was conducted to characterize the homogenized Camp Withycombe soil. These tests were conducted prior to subjecting the soil to vendor treatment and analysis. The matrix of samples subjected to chemical and physical characterization tests are provided in Table 4-1. The analytical procedures used to conduct these tests are presented in Table 4-2. A description of each test method is given below.

4.2.2.1 Physical Testing Methods

4.2.2.1.1 Permeability

Permeability is the measure of the capability of water to flow through the soil. The method used is outlined by U.S. Army Corps of Engineers (USACE) EM-1110-2-1906, App. VII. This permeability test used a falling-head fixed wall permeameter, Humboldt model HM-3891 (see Figure 4-3). The procedure consisted of saturating the soil using approximately one third of the total volume of the permeameter and slowly adding 200 grams soil. A vacuum pump was used to remove air from the sample and the standpipe was filled with water. The head of water was allowed to fall and the time elapsed was recorded. The permeability was calculated by measuring the quantity (Q) of water flowing through the soil specimen of length L. The flow was calculated by formula 4.1.

$$k_t = \left(\frac{a * L}{A * t}\right) * \ln\left(\frac{h_o}{h_1}\right) \qquad [4.1]$$

Where:

k_t = Coefficient of permeability at temperature T
a = cross- sectional area of standpipe (cm^2)
h_o = head across specimen at initial time t_o (cm)
h_1 = head across specimen at measured time t_1 (cm)
L = length of specimen (cm)
T = elapsed time between head movement (seconds)
A = cross sectional area of soil (cm^2)

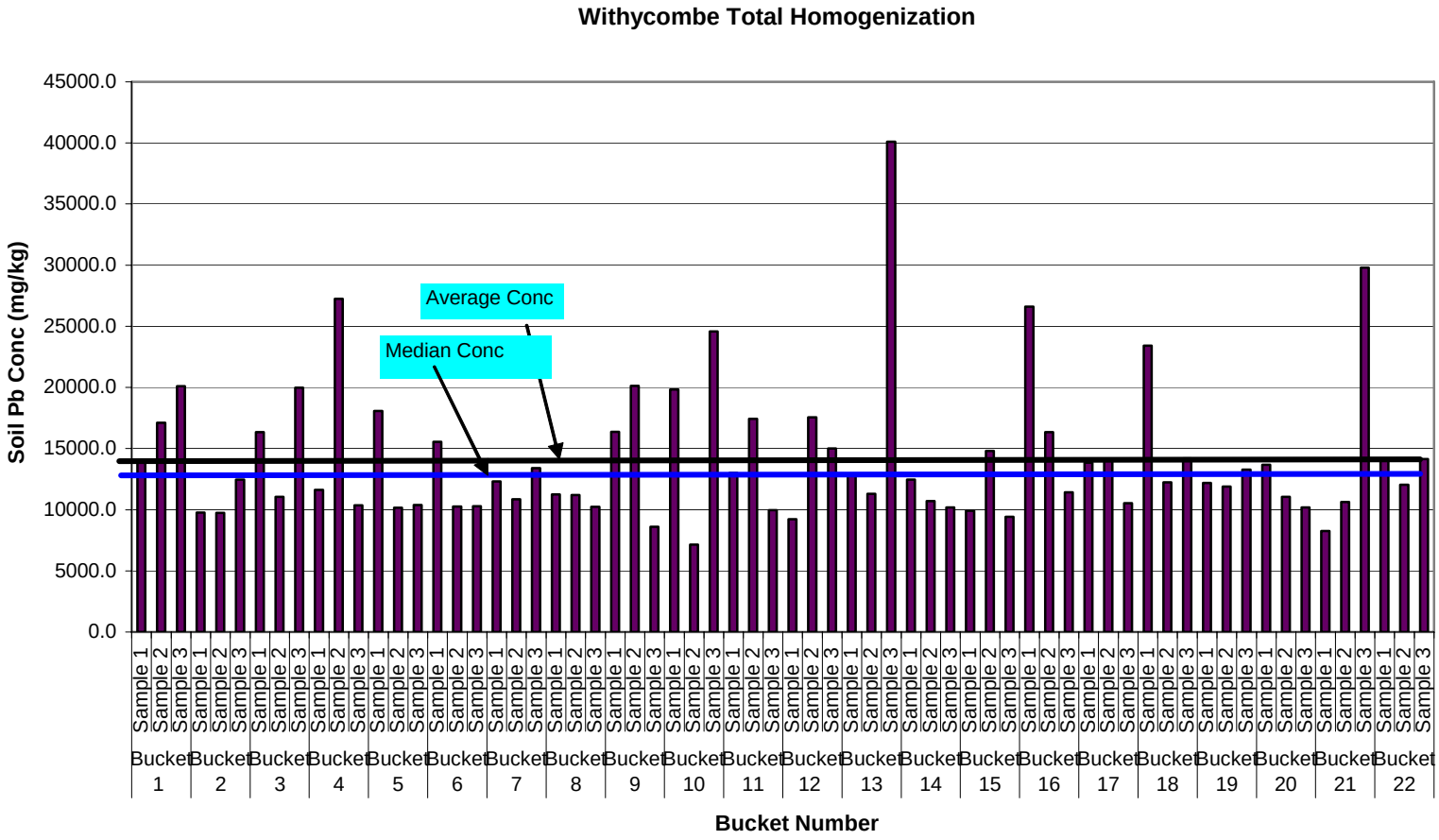


Figure 4-1. Composite soil homogenization lead data.

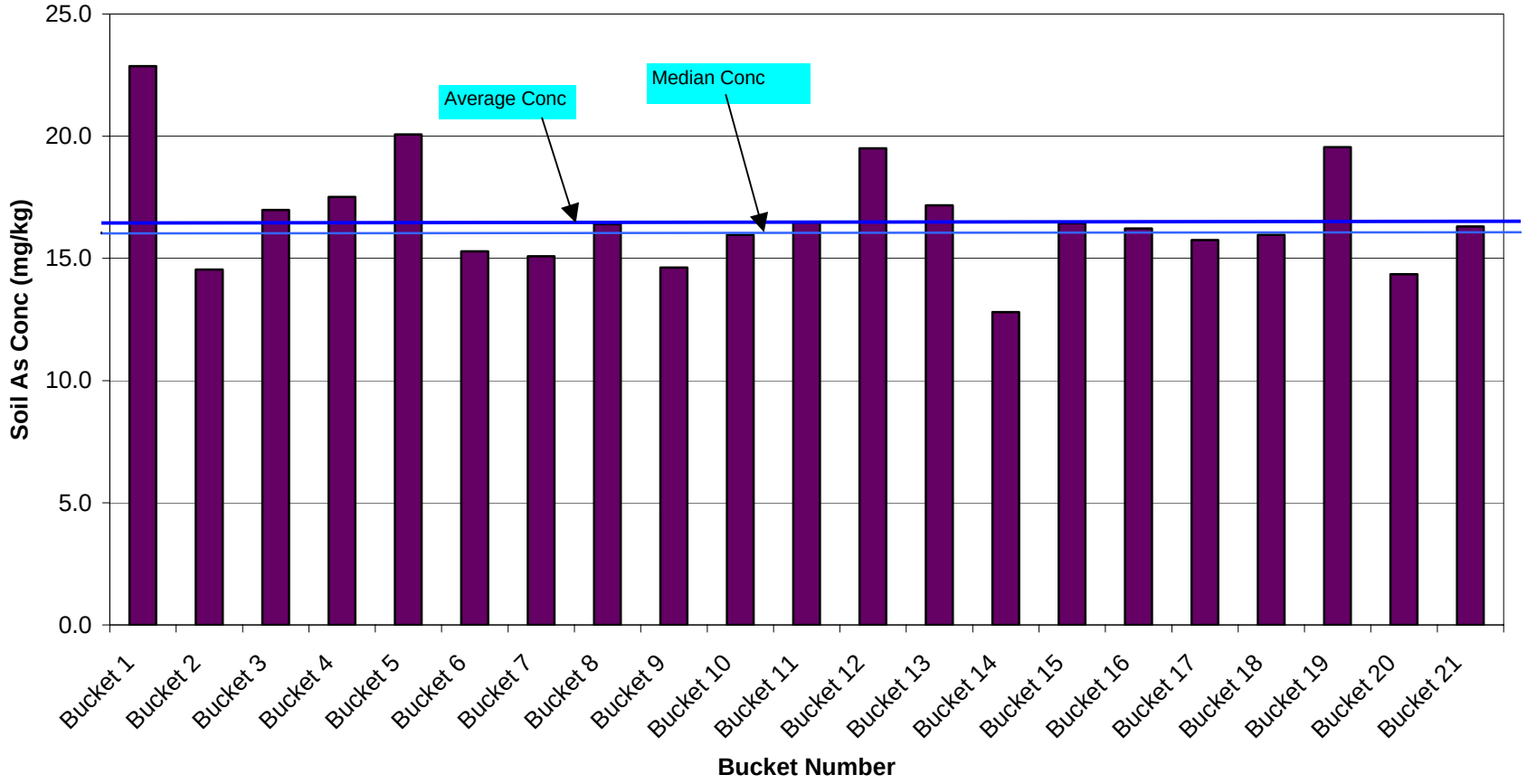


Figure 4-2. Composite soil homogenization arsenic data.

TABLE 4-1. TEST MATRIX

Test Type	Age of Sample Tested, Days
Physical Tests	
a. Cone Index	0, 14, 28,60, 120, and 360
b. UCS	0, 14, 28, 60, 120, and 360
c. Bulking	0, 14, 28, 60, 120, and 360
d. Permeability	28, 360
e. Particle Size	28
Chemical Tests	
a. Total Digestion	0, 14, 28, 60, 120, and 360
b. TCLP	0, 14, 28, 60, 120, and 360
c. SPLP	0, 14, 28, 60, 120, and 360
d. PBET	0, 14, 28, 60, 120 , and 360
c. SET	0, 14, 28, 60, 120, and 360
d. DI Leach	0, 14, 28, 60, 120, and 360
e. Phosphate	
Total phosphate	0, 14, 28, 60, 120, and 360
Leachable phosphate	0, 14, 28, 60, 120, and 360
Hydrolyzable phosphate	0, 14, 28, 60, 120, and 360
Other Tests	
a. MICROTOX®	0, 14, 28, 60, 120, & 360
b. Plant Growth and Testing	28 Day Only
c. CEC	Baseline Only
d. TOC	Baseline Only

CEC = Cation exchange capacity.
DI = Deionized.
PBET = Physiologically-Based Extraction Test.
SET = Sequential Extraction Test.
SPLP = Synthetic Precipitation Leaching Procedure.
TCLP = Toxicity Characteristic Leaching Procedure.
TOC = Total Organic Carbon.
UCS = Unconfined compressive strength.

Note: Each test was conducted as part of the baseline testing.

TABLE 4-2. METHODS AND ANALYTICAL PROCEDURES

Test	Sample Preparation	Analytical Technique
Total lead	USEPA Method 3051	USEPA Method 6010B
TCLP	USEPA Method 1311	USEPA Method 6010B
SPLP	USEPA Method 1312	USEPA Method 6010B
CEC	USEPA Method 9081	USEPA Method 6010B
Sequential Extraction		
Exchangeable	Method as outlined by Tessier	USEPA Method 7000A
Bound to Carbonates	Method as outlined by Tessier	USEPA Method 7000A
Bound to Iron and Manganese Oxides	Method as outlined by Tessier	USEPA Method 7000A
Bound to Oxides	Method as outlined by Tessier	USEPA Method 7000A
Residual	USEPA Method 3052	USEPA Method 7000A
Phosphate Analysis		
Total phosphate	USEPA Method 3051	HACH® DR/2010
Leachable phosphate	Distilled water leach	HACH® DR/2010
Hydrolyzable phosphate	USEPA Method 3051 on DI Leach	HACH® DR/2010
Permeability	Method as outlined by Mitchell	USACE EM 1110-2-1906, App. VII, Falling head permeameter
Cone Index	Compaction Method	HQDA TM 5-530
UCS	Compaction Method	Modified ASTM C109-93
Bulk density	Compaction Method	Modified ASTM C 109-93
TOC	USEPA Method 9060	USEPA Method 9060
Particle Size	Air Dried	USACE EM 1110-2-1906, App. V
MICROTOX®	DI Leach	MICROTOX® system
Plant Analysis	USEPA Method 3052 + 5ml 30% H_2O_2	USEPA Method 6010B

ASTM = American Society for Testing and Materials.
CEC = Cation Exchange.
DI = Deionized.
EM = Engineering Manual
SPLP = Synthetic Precipitation Leaching Procedure.
TCLP = Toxicity Characteristic Leaching Procedure.
TM = Technical Manual
TOC = Total Organic Carbon.
UCS = Unconfined compressive strength.
USACE = U.S. Army Corps of Engineers
USEPA = U.S. Environmental Protection Agency.

Figure 4-3. Humboldt HM-3891 permeameter.

4.2.2.1.2 Bulk Density

Bulk density is the measure of the mass per unit volume of the whole soil specimen. American Society for Testing and Materials (ASTM) D 698-91 was used as a guideline for this test but was modified to fit the needs of this study. The method used for this study consisted of using a compaction hammer to deliver a compactive force of 12,400 ft-lb/ft^3 to the soil sample. The molds required for method ASTM D 698-91 required a large volume of soil and generated a large quantity of waste. Molds from method ASTM C 109-93 were used in this study because they generated much less waste than those used in ASTM D 698-91. The samples were compacted in these molds (ASTM C 109) using the same compactive effort as specified in ASTM D 698-91.

Modifications to the compaction hammer were necessary to conduct this test. These modifications were necessary for the hammer to fit the mold and deliver the required force. The hammer was modified by attaching a 1.9- by 1.0- by 5.0-inch brass head (see Figures 4-4 and 4-5) to the end of a standard ASTM D 698-91 compaction hammer.

Figure 4-4. Modified compaction hammer used for compaction of bulk density and UCS samples.

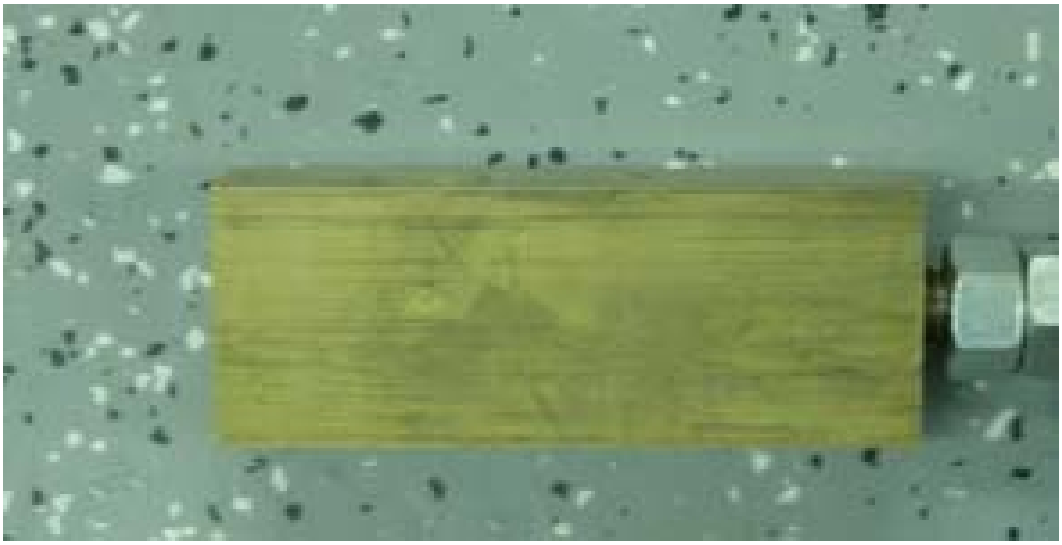


Figure 4-5. Close up view of compaction hammer head.

The ASTM C 109-93 test requires two 2- by 2- by 2-inch molds (see Figure 4-6). The molds were greased to allow the samples to be removed from the molds without fracturing. To fill the molds, one empty mold was stacked on top of another empty mold and both were attached to the baseplate. This provided a 2- by 4-inch cavity for compaction. Soil was added until each cube was three quarters full with loose soil. The soil was compacted by placing the compaction hammer on one side of the cube, raising the weight to its highest position, and dropping the weight. The hammer was rotated 90^{o} and the weight was raised and dropped again. The weight was dropped five times for each cube. The soil was then scarified to prevent layering of the soil, and additional soil was added to the molds. The second lift was compacted using mirror images of the hammer positions from the first lift. The hammer positions used for both lifts are shown in Figures 4-7 and 4-8.

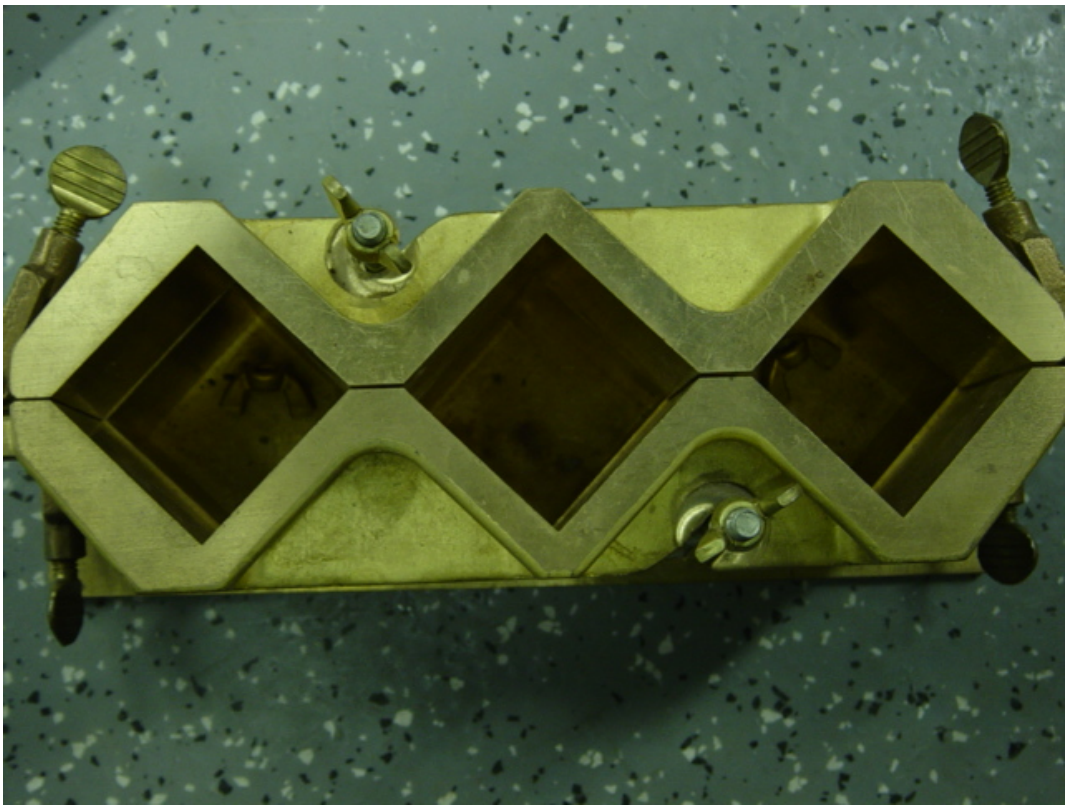


Figure 4-6. Mold for bulk density test.

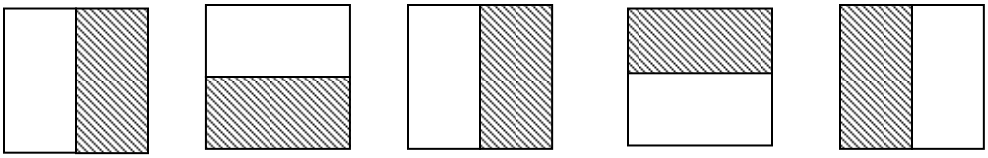


Figure 4-7. Hammer position for first lift of compactions.

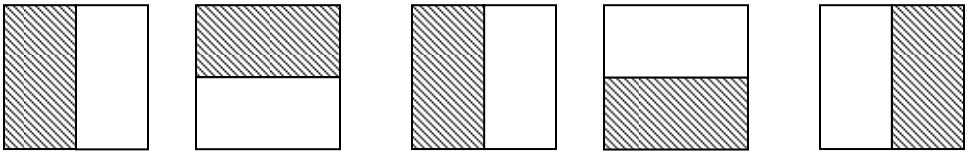


Figure 4-8. Hammer position for second lift of compactions.

After the second set of compactions had been performed, the top mold was removed and the soil was trimmed to form a 2-inch cube. The mold was disassembled and the volume of the soil was measured using a Fowler Max-Cal caliper. The soil was weighed using a Denver Instruments TL-8102D scale. The density of the soil was found by the formula:

$$\text{Density} = m/V \qquad [4.2]$$

Where:
m = mass of the soil (grams)
V = Volume of sample (cm^3)

4.2.2.1.3 Unconfined Compressive Strength (UCS)

The UCS test was used to determine the strength development characteristics of the Camp Withycombe soil. UCS measures the strength per unit area required to fracture a sample. ASTM C 109-93, was modified for this study. ASTM C 109-93, which was developed for hydraulic cements and details a tamping method to mold the specimens, was modified for this study. For this test, the same compaction method as specified in the bulk density section of this report was followed. The same samples prepared for the bulk density were used for UCS testing. The surface area for each specimen cube was determined using a Fowler Max-Cal caliper. A Tinius Olson Super-L compressive apparatus was used to supply the necessary force required to fracture the sample. The maximum strength required to fracture the sample was obtained. The UCS was calculated by using equation 4.3.

$$UCS = F/A \qquad [4.3]$$

Where:
UCS = Unconfined compressive strength (psi)
F = Force required to fracture sample (lb)
A = Area of sample (in^2)

4.2.2.1.4 Particle Size Analysis

Particle size was accomplished in two phases according to USACE EM 1110-2-1906 Appendix V. The first phase of this procedure involved passing a known mass of soil through a nest of sieves to obtain the soil's particle distribution. EM 1110-2-1906 does not specify the sieve sizes used to make up the nest. For this study, 11 sieves were used meeting the specifications shown in Table 4-3.

TABLE 4-3. SIEVE SIZES USED FOR PARTICLE SIZE ANALYSIS

12.5 mm
9.5 mm
8.0 mm
4.5 mm
2.0 mm
1.0 mm
500 μm
250 μm
125 μm
106 μm
75 μm

The second phase of particle size determination was the hydrometer analysis. The hydrometer analysis was necessary to determine the particle size distribution of soil passing the 75 μm sieve. A mass of soil passing a 75-μm sieve was placed into a graduated cylinder and 10 mL of 1 N Hexametaphosphate dispersing agent was added to the cylinder. Then, a hydrometer was placed in the solution at 0-, 4-, 15-, 30-, 60-, 120-, and 1440-minute time intervals and a hydrometer reading was obtained. The temperature was also recorded at each of these time intervals. The following formula was used to determine the percent finer by weight:

$$\text{Percent finer by weight} = (G_s/(G_s-1)) * (100/W_s)*(R-C_d+m) \quad [4.4)$$

Where:

G_s = specific gravity of the soil
W_s = oven-dry weight of soil used in hydrometer analysis (grams)
$R-C_d+m$ = corrected hydrometer reading minus dispersing agent correction plus temperature correction.

Using the particle size analysis, this soil was classified by method ASTM D 2487 *Standard Classification of soils for Engineering Purposes*.

4.2.2.1.5 Cone Index

The cone index (CI) measures a material's resistance to penetration of a 30° right circular cone. This test follows method Headquarters, Department of the Army (HQDA) TM 5-530. CI value is reported in pounds per square inch (psi). Two cones were available for this test: the first being the Waterways Experiment Station (WES) standard cone having an area of 0.5 square inches and the second being an airfield penetrometer having an area of 0.2 square inches. Because of the smaller surface area, the airfield penetrometer was capable of measuring larger CI values. This penetrometer was used for CI values reported up to 750 psi. If the force required was greater than 750 psi, the value reported was 750+ psi. The standard WES cone was used for values less than 300 psi. The cone penetrometer used in this study is shown in Figure 4-9.

Figure 4-9. Cone penetrometer.

Soil samples for CI were prepared in 4-inch cylindrical standard proctor molds. These molds measure 4 inches in diameter and 4 inches in height. Soil was placed in these molds and compacted using the ASTM compaction procedure. The penetrometer was pushed into the soil until the top surface of the cone was level with the top surface of the compacted soil. The force to meet this requirement was recorded in psi.

4.2.2.2 Chemical Analysis

4.2.2.2.1 Total Organic Carbon (TOC)

The TOC of the soil was analyzed to determine the organic carbon content of the Camp Withycombe soil. The method followed is outlined in USEPA Method 9060, *Total Organic Carbon*. The analysis was performed using a Shimadzu SSM-5000A TOC analyzer. To obtain one TOC value, two samples were needed. The first sample was used to obtain the Total Carbon (TC) of the sample, while the second sample was used to obtain the inorganic carbon (IC) of the sample. The TOC was obtained by subtracting the IC content from the TC content. The TOC procedure was performed as follows: 50-mg samples of soil were measured in a ceramic weigh boat using a Mettler Toledo model AG204 analytical scale. The weigh boat corresponding to the total carbon sample was inserted into the TC chamber and heated at 900 ^{o}C for approximately

10 minutes. The sample was removed from the Shimadzu analyzer and the second sample was placed in the IC chamber. This sample was heated at 200 ^{o}C for approximately 10 minutes. Once the TC and IC concentrations had been found, the TOC could be calculated. TOC was reported in mg/kg.

4.2.2.2.2 Cation Exchange Capacity (CEC)

The CEC of a soil gives the quantity of available sites for cations to bond to the soil. The test method used followed USEPA Method 9081. The test required passing the soil through a 2-mm sieve.

The CEC tests were performed as follows. Approximately 4 grams of sieved soil were weighed using a Mettler Toledo model AG204 scale into a 50 mL Oak Ridge centrifuge tube. Then, 33 mL of American Chemical Society (ACS) grade 1 N sodium acetate was added to the centrifuge tube. The centrifuge tube was agitated for 5 minutes and then centrifuged until the supernatant was clear. The liquid was decanted and discarded. This procedure was repeated three more times. After the sodium acetate addition had been performed, 33 mL of isopropyl alcohol was added to the sample. This step was performed to "wash" the sample of any sodium acetate solution. The sample was agitated for 5 minutes and then the sample was centrifuged until the supernatant was clear. The isopropyl alcohol was discarded after centrifuging. The addition of isopropyl alcohol was performed two more times. After this step had been performed, 33 mL of ammonium acetate was added to the centrifuge tube. The centrifuge tube was agitated for five minutes and the sample was centrifuged as before. The ammonium acetate solution was decanted into a 100 mL volumetric flask. This procedure was repeated two more times. The ammonium acetate solution was diluted to 100 mL. The extract was analyzed according to USEPA Method 9081. The CEC of the soil was reported in meq/L.

4.2.2.2.3 Total Lead

USEPA method 3051 was followed for this study to prepare the soil samples as listed in Table 4-2. Sample preparation was performed by first weighing 0.5 grams of soil into a microwave digestion vessel (Figure 4-10). Ten mL of concentrated nitric acid were added to the soil. The vessel was placed in a microwave and heated to 185 ºC for 15 minutes. The sample was cooled and vacuum filtered (Figure 4-11) using Millipore HA 0.45µm filters. The filtrate was then analyzed for total lead in accordance with USEPA Method 6010B as listed in Table 4-2.

Figure 4-10. Microwave used for sample digestion.

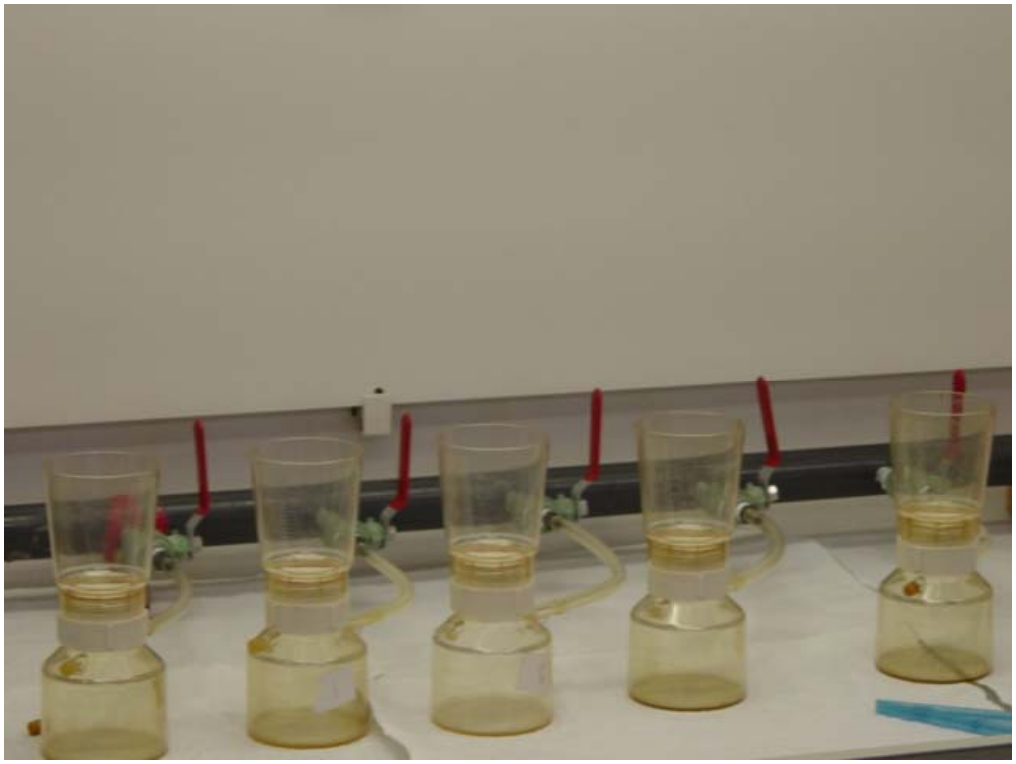


Figure 4-11. Vacuum filtration apparatus for digestion and PBETs.

4.2.2.2.4 PBET

The PBET was performed to measure the bioavailability of the lead in the soil. There was no validated standard method for the PBET, so the method outlined by Ruby Standard Operating Procedure (SOP), 4 November 1999, was used as a guideline. Ruby's method was modified for this test. Ruby's method required the samples to be subjected to a temperature controlled tumbler procedure. Ruby's procedure was modified by creating a water bath in an insulated container. Laboratory studies were conducted and it was found that over the 1 hour time period required for the extraction procedure, the temperature of the sample dropped less than 1 ºC, which was within specifications for the test. This modification was done to avoid the difficult construction of a constant temperature water bath tumbler.

The PBET used a simulated gastrointestinal fluid to perform the extraction. There were two possible extraction fluids for this test. Both extraction fluids were made of a 0.4 M glycine solution with the pH adjusted to 1.5 and 2.3 with HCl. When the lab study tests were being performed, PBET was undergoing validation for use in estimating the relative bioavailability of lead for contaminated soils. The PBET had been correlated to animal feeding studies using swine as subjects. Unfortunately at the time of this study, only swine feeding studies using lead paint contaminated soil had been completed. This test used the 1.5 pH extract. Later studies indicated that the PBET test correlations to swine studies may be dependent upon the lead complex that had formed in the soil. Ongoing tests at a 2.3 pH solution indicated that the 2.3 pH may be more appropriate for the treated soil analyses. As a result of the correlation conflicts identified in the correlation studies, extract solutions at both pH values were used in this study to provide an indication of bioavailability reduction.

The PBET procedure consisted of using one hundred milliliters of either the 1.5 or 2.3 pH solutions and pouring it into a high density polyethylene (HDPE) 125 mL sample bottle. The sample bottle was then heated to 37 ^{o}C. Tap water was also heated to this temperature. One gram of soil was weighed using a Mettler Toledo AG204 scale. The soil was placed in the sample bottle and the sample bottle was placed into an insulated container. The 37 ^{o}C tap water was poured into the annulus of the insulated container. The container was sealed forming a water bath for the sample. The container was tumbled in an end-over-end fashion for one hour. Prior to cooling, the sample bottle was removed from the insulated container. The extract was filtered using vacuum filtration and passed through a Millipore HA 0.45µm filter. The extract was analyzed for lead according to USEPA Method 6010B as specified in Table 4-2.

4.2.2.2.5 TCLP

The TCLP is a regulatory test used to determine quantities of leachable compounds that can leach to groundwater or to the environment at levels that can be dangerous to animals and humans. For lead, the regulatory level for the waste to be regulated as hazardous is ≥5 mg/L. As previously stated, in addition to hazardous criteria of ≥5 mg/L, the Universal Treatment Standard (UTS) of ≥0.75 mg/L of lead in the TCLP leachate is also a performance metric. For this study vendor treatments must pass the <0.75 mg/L lead UTS performance metric.

A modified USEPA Method 1311 was used for TCLP sample preparation. The method specifies using a 100 gram sample of soil. This quantity of soil produces a large volume of extract and uses a large amount of sample. MSU decided to scale down the soil sample mass to 12.5 grams of soil to reduce the amount of soil required for the test and to reduce the extract generated as a result of performing the extraction. No other modifications of the extraction method were made.

Prior to starting the extraction, the soil was ground and passed through a 9.5 mm sieve. A pretest with two extraction fluids was performed on this soil to determine the buffering capacity of the soil. Extraction fluid No. 1 consisted of adding 5.7 mL glacial acetic acid to 500 mL ASTM D1193-91, Type 1 water, adding 64.3 mL sodium hydroxide, and diluting to 1 L with ASTM D1193-91, Type 1 water. Extraction fluid No. 2 consists of diluting 5.7 mL glacial acetic acid to 1 L with ASTM D1193-91, Type 1 water. The first extraction fluid had a pH of 4.95 and the second extraction fluid had a pH of 2.88.

Based on the pretest, all samples in this study were prepared using extraction fluid No. 1. Extract samples were prepared by weighing 12.5 grams of sample using a Mettler Toledo AG 204 balance. The soil was placed in a 250 mL HDPE sample container and 250 mL of extraction fluid was added to the soil. The soil and extract solution was tumbled end-over-end for 18 hours. At the completion of this tumbling period, the samples were vacuumed filtered using a Whatman Glass Fiber Filter (GF/F) 0.70-µm filter. After filtration, the samples were preserved by the addition of 1.0 mL ACS grade concentrated nitric acid. The samples were analyzed using USEPA method 6010B as specified in Table 4-2.

4.2.2.2.6 SPLP

The SPLP evaluated the potential for leaching of lead and other soil or waste constituents subject to acid rain conditions. USEPA Method 1312 was followed except that, as discussed with the TCLP method, 12.5 grams of soil were extracted rather than the full 100 gram samples. A summary of the method follows.

For the SPLP, one of two possible extraction fluids could be used. This was dependent on where the waste originated. If a waste originated east of the Mississippi River then the pH of the extraction fluid would be 4.2. If the waste originated west of the Mississippi River, then the pH of the extraction fluid would be 5.0. Because Camp Withycombe is located west of the Mississippi River, the pH 5.0 extraction fluid was utilized for all SPLP tests. The extraction fluid consisted of a 60/40 wt% mixture of sulfuric: nitric acid diluted with ASTM D1193-91, Type 1 water to a final pH of 5.00 +/- 0.05.

Soil samples were prepared by first passing the soil through a 9.5 mm sieve. The soil was placed in the extraction fluid and tumbled for 18 +/-2 hours. The samples were filtered using a Whatman GF/F 0.70-µm filter. The samples were preserved by the addition of concentrated nitric acid. The samples were analyzed using USEPA method 6010B as specified in Table 4-2.

4.2.2.2.7 Distilled Water Leach

A distilled water leach was performed on the samples to provide extract for use in MICROTOX®, leachable phosphate, and hydrolyzable phosphate analyses. The first step in the extraction was to weigh 12.5 grams of Camp Withycombe soil into a 250 mL HDPE sample bottle using a Mettler Toledo AG204 scale. The same 20:1 liquid to solids ratio discussed in section 4.2.2.2.5 was used in this extraction. Two hundred and fifty mL of distilled water was added to the 250 mL sample bottle. The bottle was tumbled end-over-end for 18 +/-2 hours. The extract was filtered using a Whatman 0.7-µm GF/F filter. The extract was stored and used for the tests mentioned above.

4.2.2.2.8 SET

The sequential extraction procedure partitioned particulate trace metals, including lead, to provide a relative measure of how tightly the metals were bound to the soil. This method consisted of subjecting the soil to five extractions. The extractions in this procedure were exchangeable metals, metals bound to carbonates, metals bound to iron and manganese oxides, metals bound to organic matter, and residual metals (Tessier).

The method outlined by Tessier was used as guidance in this study with one modification. The fifth extraction in Tessier's method required adding hydrofluoric acid (HF), heating the sample until almost dry, and then adding additional hydrofluoric acid to the sample. This extraction step was repeated twice. The fifth extraction procedure used large quantities of HF and was very time consuming. After a thorough search for alternative HF extraction methods, MSU determined that a hydrofluoric digestion, as specified in USEPA Method 3052, would be comparable to that specified by Tessier. Method 3052 was substituted for the HF method specified by Tessier because it was faster to implement and much safer. The SET procedure used for this study is outlined below.

Approximately one gram of soil was placed in a 50 mL Oak Ridge polypropylene centrifuge tube and the weight was measured using a Mettler Toledo AG204 analytical scale. This soil sample was sequentially extracted 5 times. The soil was "washed" between each step by adding distilled water and tumbling end-over-end for 30 minutes. The sample was centrifuged at 2500 rpm for 30 minutes and the water was discarded. Specific procedures for each fraction extraction are described below:

Fraction No. 1 - Exchangeable

After the soil had been placed in the 50 mL polypropylene centrifuge tube, 8 mL of a 1.0 M magnesium chloride solution was added to the centrifuge tube. The centrifuge tube was tumbled end-over-end for 1 hour. After tumbling, the sample was centrifuged at 2500 rpm for 30 minutes. When the centrifugation was completed, the extract was decanted and analyzed as specified in Table 4-2. The soil was washed as previously described and the washed soil was used in Fraction No. 2.

Fraction No. 2 - Bound to Carbonates

The extraction fluid for step No. 2 consisted of 1.0 M sodium acetate adjusted to a pH of 5.0 with acetic acid. Eight mL of this extraction fluid were added to the centrifuge tube containing the solid from fraction No. 1. The sample was tumbled as previously described for a total of 5 hours. The sample was then centrifuged at 2500 rpm for 30 minutes and the extract decanted and saved. The extract was analyzed as specified in Table 4-2.

Fraction No. 3 - Bound to Iron and Manganese Oxides

The extraction fluid for step No. 3 was a 0.04 M hydroxylamine hydrochloride solution with 25 percent by volume of acetic acid. The extraction fluid was added to the centrifuge tube containing the washed solid from fraction No. 2. The sample was heated in a constant temperature water bath at 93 +/- 3 ^{o}C for 6 hours. After the sample was removed from the water bath, it was allowed to cool. The sample was centrifuged at 2500 rpm for 30 minutes. The extract was decanted and saved. The extract was analyzed as specified in Table 4-2.

Fraction No. 4 - Bound to Organic Matter

The extraction fluid used in step No. 4 consisted of 5 mL of a 30 percent hydrogen peroxide solution adjusted to a pH of 2 with nitric acid added to 3 mL of a 0.02 M nitric acid solution. The extraction fluid was added to the washed soil from fraction No. 3. The sample was placed in a constant temperature water bath at 85 +/- 2 ^{o}C for 2 hours. After two hours, a second addition of hydrogen peroxide modified to a pH of 2 with nitric acid was added to the sample and heated to 85 +/- 2 ^{o}C for 3 hours. The mixture was allowed to cool and 5 mL of 1.2 M ammonium acetate in 20 percent (vol/vol) nitric acid was added to the sample. The sample was diluted to 20 mL with ASTM D1193-91, Type 1 water and tumbled in an end-over-end fashion for 30 minutes. The sample was centrifuged at 2500 rpm for 30 minutes. The extract was saved and analyzed as specified in Table 4-2.

Fraction No. 5 - Residual

Step No. 5 required a transfer of the soil remaining from step No. 4 to a microwave digestion vessel. This required a minimal amount of distilled water. After the soil had been transferred to the digestion vessel, 9 mL of nitric acid and 5 mL of hydrofluoric acid were added to the vessel. The sample was heated in the microwave (see Figure 4-10) at 185 ^{o}C for 9.5 minutes as specified by USEPA Method 3052. The sample was then filtered by vacuum filtration using a Millipore 0.45-µm filter (see Figure 4-11). The extract was diluted to 100 mL and analyzed for lead as specified in Table 4-2.

4.2.2.2.9 Phosphate Analysis

Three forms of phosphate were determined from this test. The types of phosphate analyzed were: total phosphate, leachable phosphate, and acid hydrolyzable phosphate. The descriptions of the tests are given below.

4.2.2.2.9.1 Total Phosphate. Total phosphate analysis provided an indication of the quantity of phosphate contained in the soil. Total phosphate analysis was performed by using the extract from the nitric acid digestion USEPA method 3051. The extract was poured into a vial and the vial was placed in a HACH® DR/2010 spectrophotometer (shown in Figure 4-12). The instrument was zeroed to account for any color differences between samples. A packet of solid ammonium molybdate and antimony potassium tartrate, supplied by the HACH Corporation, was then poured into the vial. This solid reacted with the phosphate in the solution by turning bluish in color. The color intensity is directly proportional to the phosphate concentration. The calibrated spectrophotometer gave a direct phosphate reading based on the change in opacity of the sample.

Figure 4-12. HACH® DR/2010 spectrophotometer.

4.2.2.2.9.2 Leachable Phosphate. Leachable phosphate provided an indication of the concentration of phosphate that was water soluble and had the potential to impact surface runoff. The concentration of leachable phosphate was determined by first performing a distilled water extraction on the soil as described in section 4.2.2.2.7. The extract was used to determine the leachable phosphate concentration of each sample. This was accomplished by pouring the extract into a vial and the phosphate concentration was measured as stated in 4.2.2.2.9.1 for the total phosphate analysis.

4.2.2.2.9.3 Acid Hydrolyzable Phosphate. The acid hydrolyzable phosphate concentration was the amount of phosphate that was dissolved in solution, but not readily available for reaction due to complexation. Aggressive conditions are necessary to free hydrolyzable phosphate. The hydrolyzable phosphate concentration was determined by performing a nitric acid digestion (USEPA Method 3051) on the distilled water leachate described above. This sample was then poured into a vial and placed in a HACH® DR/2010 spectrophotometer and analyzed as previously described.

4.2.2.3 Other Characterization Tests

4.2.2.3.1 MICROTOX®

The MICROTOX® test was conducted to provide a measure of the toxicity of the soil to a specific strain of bacteria. The specific strain of bacteria used in this test is *vibrio fischeri*. MICROTOX® uses a decrease in luminescence of *vibrio fischeri* bacteria to determine the effective concentration (EC50) of a sample to kill 50 percent of the bacteria.

For this procedure, a 20 percent sucrose solution prepared with the distilled water leach extract was used to prevent a phenomenon known as hormesis. Hormesis is caused by a strain on the bacteria that causes the bacteria to emit a higher quantity of light than normal and is often caused by exposure of the bacteria to heavy metals. The sucrose provided a food source for the bacteria and inhibited this phenomenon.

The procedure consisted of placing glass cuvettes in the MICROTOX® system (Figure 4-13). A diluent solution provided by Strategic Diagnostics was poured into half of the cuvettes. The leachate solution from the DI leach was poured into one of the cuvettes containing diluent. The sample containing the DI leachate was diluted into other cuvettes containing diluent using serial dilutions. The bacteria were placed in the other half of the cuvettes that contained no sample. The initial light intensity was measured for each cuvette containing bacteria. The diluted leachate solutions were poured into the cuvettes containing bacteria. After 15 minutes, the light intensity was measured again. Based on the decrease of light from each cuvette, an EC50 of each test specimen was determined.

Figure 4-13. MICROTOX® system.

4.2.2.3.2 Plant Analysis

Although the MICROTOX® test provided a relative indication of the toxicity of the soil and the PBET provided an indication of the bioavailability of the lead if ingested, a test was needed to indicate the bioavailability of lead in the environment. After a thorough review of the existing bioavailability methods, MSU determined that a method indicating lead accessibility to plants was needed.

The first step in developing a plant bioavailability test was to conduct a screening test to determine if plants could be established in the Camp Withycombe soil. As part of the screening, a phosphate free water-soluble fertilizer was applied to half of the plants used in the screening test.

The next step in the development of the test was to identify plant species that would be effective in accumulating lead. A total of over 200 plant species were identified as possible candidates for the study and narrowed to 4 species to use in the screening phase. The four types of plants included Brassica Juncea (Indian Mustard), Pisum Sativum (Snow Pea), Arabidopsis Thaliana (Moose-Ear Cress), and Triticum Aestivum (Wheat) (see Figure 4-14). These plants were identified by the MSU Plant and Soil Science Department as plant species with the ability to "take up large quantities of lead."

Seeds of each of the four plants were placed at a depth of approximately 1/2 inch in 4-inch plastic pots filled with Camp Withycombe soil. Six replicates of each identified plant species were planted in the untreated Camp Withycombe soil. Three replicates of each plant

were fertilized and three were not. Those pots containing the seeds were watered and placed in a temperature and humidity controlled growth chamber. The growth chamber was necessary because the plants selected were cool weather plants. The temperature was held at approximately 68 ^{o}F and the humidity at approximately 60 percent. The chamber used a series of fluorescent lights, which were used to simulate daylight. The plants were grown in the chamber using a "short day" cycle because the selected plants were better suited for cooler climates. During a "short day" cycle, the growth lights were used for 10 hours and turned off for 14 hours. The plants were watered once daily using water containing fertilizer and water without fertilizer. The plants were randomly distributed as shown in Figure 4-14.

As observed in Figure 4-14, the four species evaluated grew at different rates. Arabidopsis Thaliana did not emerge, but the remaining three species did. These plants were allowed to grow for 28 days. After 28 days of growth, the plants were harvested. The plants were washed thoroughly to remove any dust and heated at 60 ^{o}C for 24 hours to dry the plants. The plants were extracted using the method specified in Table 4-2. USEPA Method 3052 was used for the extraction with 30 percent hydrogen peroxide added to the HF. The hydrogen peroxide was added to break down organic plant matter. The extracted plant samples were filtered using Millipore HA 45-µm filters. The extract was analyzed as specified in Table 4-2. Based on the results of the initial plant-screening phase, the optimal plant types (Pisum Sativum and Brassica Juncea) were selected and used for the vendor study.

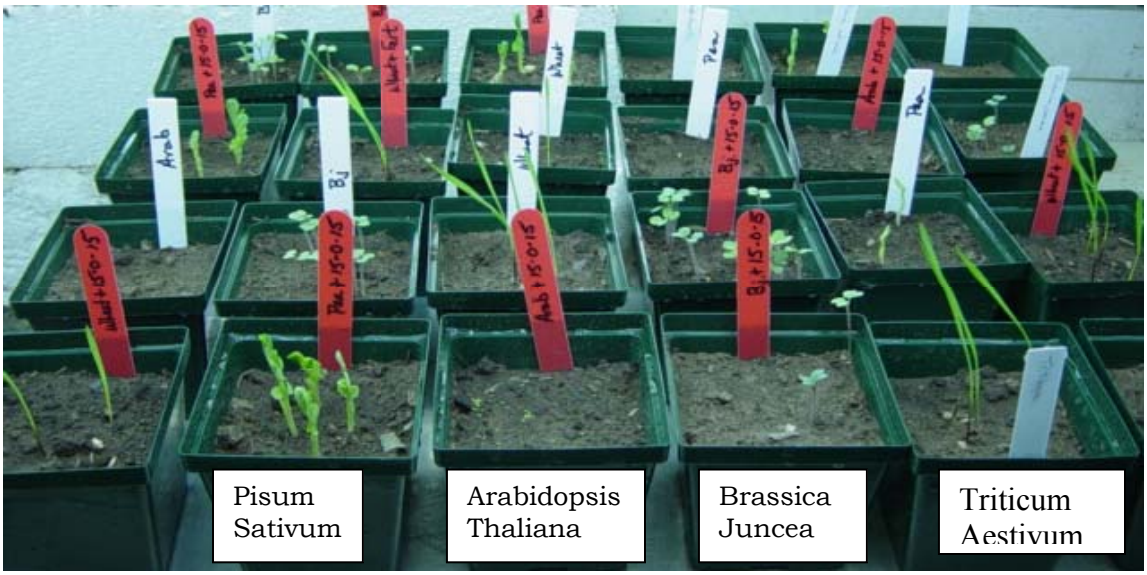


Figure 4-14. Four types of plants being tested for lead uptake.

4.3 Generic Phosphate Screening Treatment of the Soil

Various phosphate types were selected and screened as part of a research project conducted at MSU (Darnell). This work was conducted as part of Mr. Jason Darnell's thesis that he completed for his Master of Science degree. In this effort, Darnell conducted a review of all currently used phosphate treatments. Darnell selected the seven most promising types of

phosphate and dosages to be tested in his laboratory evaluation based on the information obtained during his thesis literature review. The phosphates types and dosages he evaluated in the laboratory study are presented in Table 4-4. Using the chemical results of this phosphate screening study and focusing on the minimum TCLP and phosphate leaching results, he selected hydroxyapatite at the stoichiometric ratio of 4 X (0.12 M) to be evaluated as one of the treatments for the Camp Withycombe study. This treatment is referred to as the Lab treatment throughout the remainder of this report. Details of this screening procedure are provided by Darnell.

4.4. Vendor Treatment of the Soil

For each vendor process, 5-gallon samples were mixed in a Hobart No. C-600 mixer for 10 minutes prior to amendment addition. After mixing, the amendments were slowly added to the soil and stirred for 5 minutes. Descriptions of each vendors' amendments are listed in Table 4-5. After 5 minutes, the mixer was stopped and the sides of the mixer were scraped to remove any clumped soil. The soil was then stirred for 5 more minutes. After the samples were stirred, the soil was removed. Bulk density and CI samples were prepared using compaction as previously described. The CI samples were retained in the molds. The bulk density samples were removed from the compaction molds. The bulk density and CI samples along with the remaining treated soil were stored in plastic containers in a humidity chamber. These samples were stored at room temperature and 95 percent relative humidity (RH) until required for testing.

All samples were cured initially for 24 hours prior to any testing. After this 24 hour period the testing was initiated and these samples were termed the day 0 samples. Testing was conducted in triplicate on each sample at 0, 14, 28, 60, 120, and 360 days of aging. The cured samples were subjected to chemical and physical testing as outlined in Figure 3-1. A total of eight metals (silver, arsenic, chromium, copper, lead, nickel, antimony, and zinc) were analyzed in each extract sample except for the plant and PBET tests where only lead is analyzed. Results of these tests are presented in section 7 of this report.

TABLE 4-4. PHOSPHATE TREATMENTS FOR GENERIC STUDY

Hydroxyapatite
Calcium Phosphate
Sodium Phosphate
Potassium Phosphate
Phosphoric Acid
Bone Ash
Bone Char

TABLE 4-5. VENDOR TREATMENT MIXES

Vendor	Soil Weight, lb	Water Weight, lb	Additive No. 1 Description[a]	Additive No. 1 Weight, lb	Additive No. 2 Description	Additive No. 2 Weight, lb
Control	52	0	NA	NA	NA	NA
Vendor A	50	8.35	Dry grey powder	7.25	Liquid	0.3 (125mL)
Vendor B	50	5	Pellets[c], green/Grey color Approx. 1/8" diameter	1.65	NA	NA
Vendor C	50	4.55[b]	Dry powder, slow release PO_4	1.75	NA	NA
Vendor D	50	2.5	Dry grey powder	3.25	NA	NA
Generic	50	7	White powder Hydroxyapatite	9.9	NA	NA

[a]The vendors have not provided any detailed information concerning the composition of the additives. Submittal of this information will be required prior to consideration for selection for field demonstrations.

[b]The amount of water added was based on the Metals Treatment Technologies representative's visual observations as opposed to a prescribed amount based on the weight or volume of the treated material.

[c]Based on visual observations, the pellets were uniformly mixed within the soil sample. No dissolution of the pellets was observed during the mixing process. The material appears to be similar to common slow release fertilizer pellets.

NA = Not applicable.

5.0 BASELINE CHARACTERIZATION RESULTS

5.1 Soil Metal Baseline Characterization

After soil homogenization was determined to be satisfactory as described in section 4.1 of Materials and Methods, one 5-gallon bucket of soil was selected at random for baseline characterization. This baseline characterization was conducted to provide the vendors with soil data for their testing purposes.

To characterize the soil for metals concentration, 16 discrete soil samples were collected from the bucket. The results of the metals analyses for these samples are presented in Table 5-1. Average and median values were calculated with any data points exceeding the average plus three standard deviations excluded. The average concentrations of antimony, and silver were below the method detection limit (MDL). The MDLs for the contaminants of interest for this study are listed in Appendix B**.**

To determine which of these metals may be an environmental concern at Camp Withycombe and should be included in the analyses throughout the remainder of the treatability study, the metals concentration values in Table 5-1 were compared to the Oregon soil cleanup levels (residential), the Oregon ecological risk assessment level II screening level values (SLV), and USEPA Region 9 preliminary remediation goals (PRG) (residential) summarized in Table 5-2 (OAR; USEPA, 2002; and ODEQ). Residential soil cleanup levels were used for a conservative comparison because the end use of the site had not yet been determined. Lead concentrations, as expected, were above the residential soil cleanup levels and all of the ecological SLVs. Copper concentrations in the soil were above all ecological SLVs. Zinc and chromium concentrations were above ecological SLVs for plants, inverts, and birds. Nickel concentrations were above the ecological SLV for plants only. The analysis of the initial homogenized samples (Figure 4-2) shows arsenic concentrations to be of measurable concentrations using USEPA Method 7010. The analysis of the baseline samples for arsenic indicated that the average measurable concentration of arsenic was 6.73 mg/kg (Table 5-1). This was above the soil cleanup values listed in Table 5-2. Although antimony was not detected above the MDL in the baseline characterization, this metal was added to the list to be carried through the study's analyses because it is a constituent of small arms ammunition and may possibly be encountered in the field. Based on the result of the baseline metals characterization, the following seven metals were carried through all analyses (except PBET and the plant analysis): antimony, arsenic, chromium, copper, lead, nickel, and zinc.

5.2 Baseline Characterization

The purpose of the baseline characterization was to provide the vendors with background information on the soil they were to test. Thus, the primary focus of baseline testing was to generate data pertaining to the lead contained by the soil. A total of nine chemical tests and four physical tests were conducted as part of the baseline analysis. Average results for the chemical tests are provided in Table 5-3 and the average results for the physical tests are provided in Table 5-4.

TABLE 5-1. BASELINE METALS CONCENTRATION, MG/KG - DRY WEIGHT

Sample ID	Antimony	Arsenic	Chromium	Copper	Lead	Nickel	Silver	Zinc
1	< MDL	6.98	22.1	1,040.6	8,836.9	40.1	< MDL	210.8
2	< MDL	8.96	22.3	965.2	7,286.4	32.8	< MDL	200.5
3	< MDL	6.49	26.8	**10,133.7**[a]	12,336.1	38.7	< MDL	**953.8**
4	< MDL	8.37	22.9	975.6	10,713.6	37.9	< MDL	198.8
5	< MDL	5.62	20.9	946.2	7,327.4	32.0	< MDL	179.7
6	5.01	**13.64**	20.8	986.0	20,805.7	37.9	< MDL	212.7
7	**11.88**	**18.55**	21.9	**2,417.3**	**93,552.8**	26.7	**7.84**	205.4
8	**78.91**	**13.22**	11.3	456.8	**47,259.5**	15.9	< MDL	95.5
9	**69.44**	4.64	19.7	700.7	**68,285.7**	28.3	< MDL	179.4
10	< MDL	5.69	9.1	445.9	4,220.7	15.5	< MDL	92.0
11	< MDL	< MDL	22.9	814.3	8,095.8	34.1	< MDL	192.6
12	< MDL	8.35	22.8	1,030.9	9,787.2	38.8	< MDL	219.7
13	< MDL	**19.20**	26.0	882.8	14,303.7	36.2	< MDL	206.4
14	**145.54**	4.42	20.0	893.8	19,469.3	32.2	< MDL	185.8
15	4.73	10.80	22.2	1,538.0	10,399.3	34.1	< MDL	214.0
16	< MDL	8.35	22.4	854.0	18,242.9	36.2	< MDL	194.7
Average	< MDL	**6.73**	**20.9**	**895.1**	**11,678.8**	**32.3**	< MDL	**185.9**
Median		**6.73**	**22.1**	**920.0**	**10,399.3**	**34.1**		**198.8**
St. Dev.		**2.38**	**4.6**	**265.3**	**5,126.0**	**7.5**		**39.3**

[a]All left justified, bold values exceed the average plus three standard deviations of the data set and are excluded from the average, median and standard deviation values.
[b]These values are below the MDL determined for the MSU ICP.

MDL = Method detection limit.

TABLE 5-2. CONTAMINANT SCREENING LEVELS

Metal Contaminant	ODEQ Soil Cleanup Level[a], mg/kg	ODEQ Level II SLVs, mg/kg				USEPA Region 9 PRG[a], mg/kg
		Plants	Inverts	Birds	Mammals	
Antimony	NA	5	NA[b]	NA[b]	15	31
Arsenic	0.4	10	60	10	29	0.39
Chromium	1,000	1	0.4	4	3.4×10^5	1.0×10^5
Copper	10,000	100	50	190	390	3,100
Lead	200	50	500	16	4,000	400
Nickel	5,000	30	200	320	625	1,600
Silver	5	2	50	NA[b]	NA[b]	390
Zinc	NA[b]	50	200	60	20,000	23,000

[a]The post cleanup end use of the site is not known; therefore, for screening purposes, residential soil cleanup levels and PRGs were used for comparison to the metals concentrations in the soil.
[b]NA = Numerical cleanup or screening values have not been established.

ODEQ = Oregon Department of Environmental Quality.
PRG = Preliminary remediation goals.
SLV = Screening level value.
USEPA = U.S. Environmental Protection Agency.

TABLE 5-3. AVERAGE BASELINE CHEMICAL DATA FOR CAMP WITHYCOMBE SOIL

Test	Average Concentration or Value	Units	Standard Deviation
Soil Total Metals Concentrations			
Lead	11,700	mg/kg	5130
Antimony	<MDL	mg/kg	-------
Arsenic	6.73	mg/kg	2.38
Chromium	20.9	mg/kg	4.60
Copper	895	mg/kg	256
Nickel	32.3	mg/kg	7.50
Zinc	39.3	mg/kg	39.3
Soil TCLP Concentrations			
Lead	316	mg/L	38.2
Antimony	1.075	mg/L	2.07
Arsenic	0.14	mg/L	0.81
Chromium	<MDL	mg/L	-------
Copper	5.73	mg/L	0.85
Nickel	0.206	mg/L	0.011
Zinc	2.07	mg/L	0.037
Soil SPLP Concentrations			
Lead	2.92	mg/L	0.345
Antimony	0.386	mg/L	0.009
Arsenic	<MDL	mg/L	-------
Chromium	<MDL	mg/L	-------
Copper	<MDL	mg/L	-------
Nickel	<MDL	mg/L	-------
Zinc	0.194	mg/L	0.011
PBET			
pH 1.5	61.7	mg/L	7.2
pH 2.3	57.1	mg/L	6.1
Phosphate			
Total	30.7	mg/kg	5.73
Leachable	2.46	mg/kg	0.518
Hydrolyzable	7.218	mg/kg	1.30
MICROTOX®	6.78	% effect	2.03
pH	4.68		0.04
TOC	17458	ppm	4091
CEC	6.27	meq/L	0.211

CEC = Cation exchange capacity.
MDL = Method detection limit.
PBET = Physiologically-Based Extraction Test.
SPLP = Synthetic Precipitation Leaching Procedure.
TCLP = Toxicity characteristic Leaching Procedure.
TOC = Total Organic Carbon.

TABLE 5-4. BASELINE PHYSICAL PROPERTIES FOR CAMP WITHYCOMBE SOIL

Test	Average Value	Units	Standard Deviation
UCS	16.8	psi	2.9
CI	150	psi	6.3
Density	1.61	g/cm^3	0.01
Permeability	5.54E-06	cm/s	1.36E-06

CI = Cone index.
UCS = Unconfined compressive strength.

5.2.1 Baseline Chemical Analysis Results

Five baseline soil samples were subjected to a variety of chemical analytical tests. The average soil results for the pH, TOC, CEC, TCLP, and SPLP extractions are presented in Table 5-3. The pH, TOC, and CEC of five untreated soil samples is graphically presented in Figures 5-1 through 5-3, respectively. TCLP and SPLP leachates analysis of each sample were tested for the metal contaminants of interest and the resulting data are provided in Figures 5-4 through 5-6. If the analysis result for a particular metal was below the MDL, then that metal was not included in the figures.

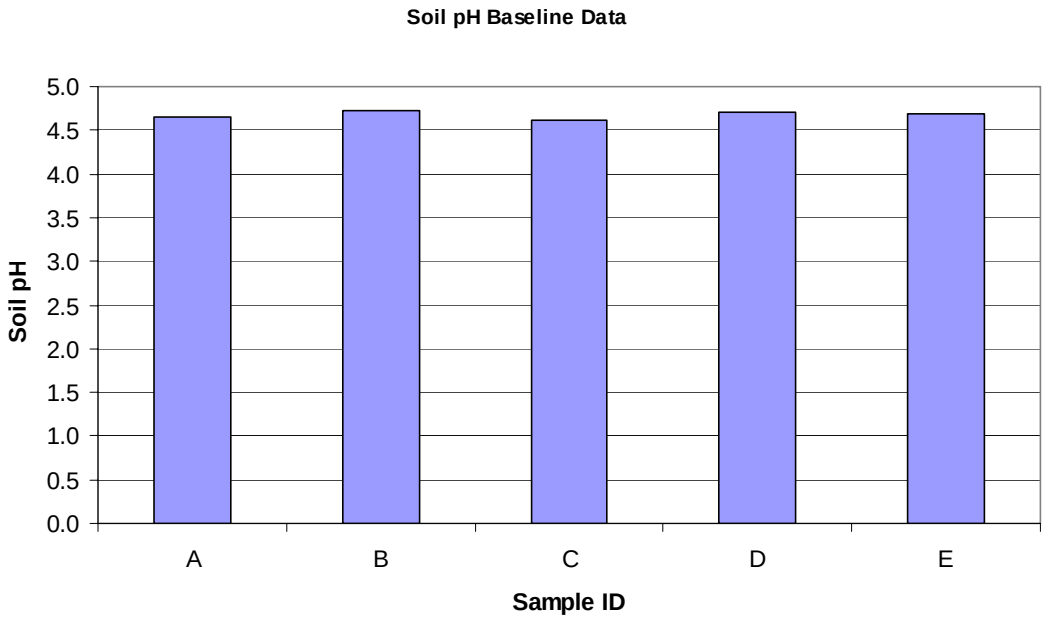


Figure 5-1. Baseline soil pH.

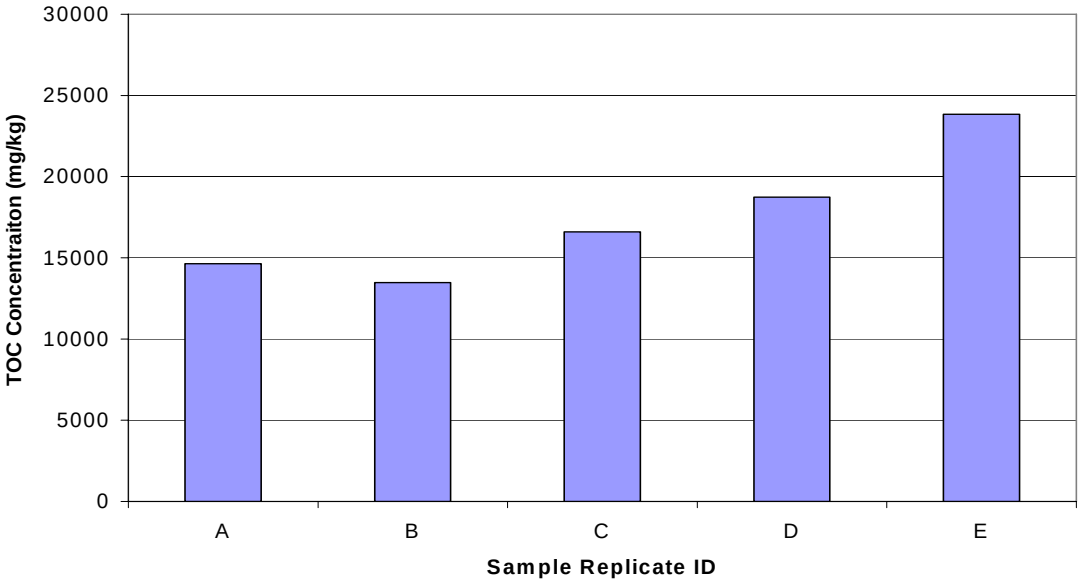


Figure 5-2. Baseline soil TOC.

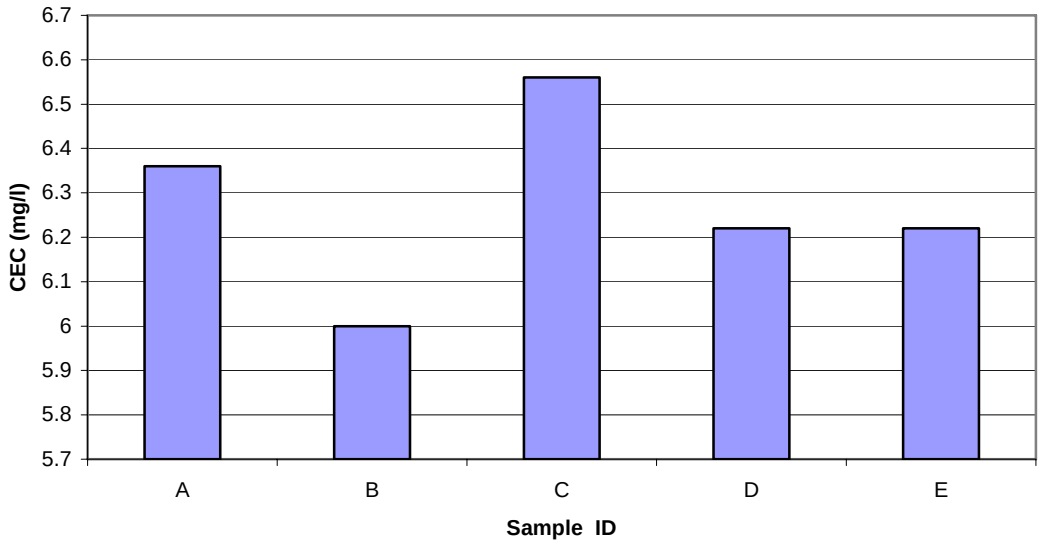


Figure 5-3. Baseline soil CEC concentrations.

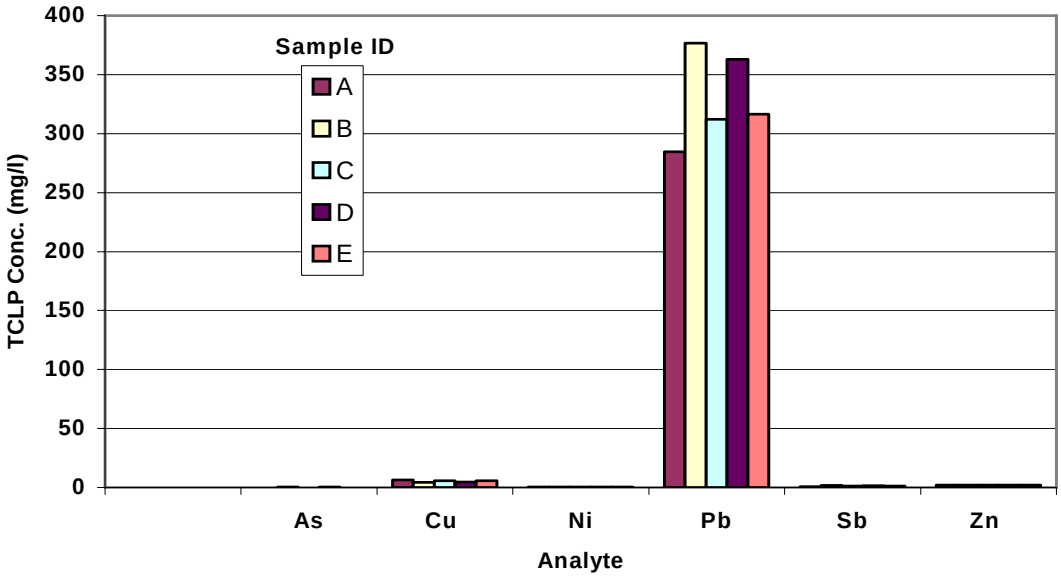


Figure 5-4. Baseline TCLP concentrations (scale 0 to 400 mg/L).

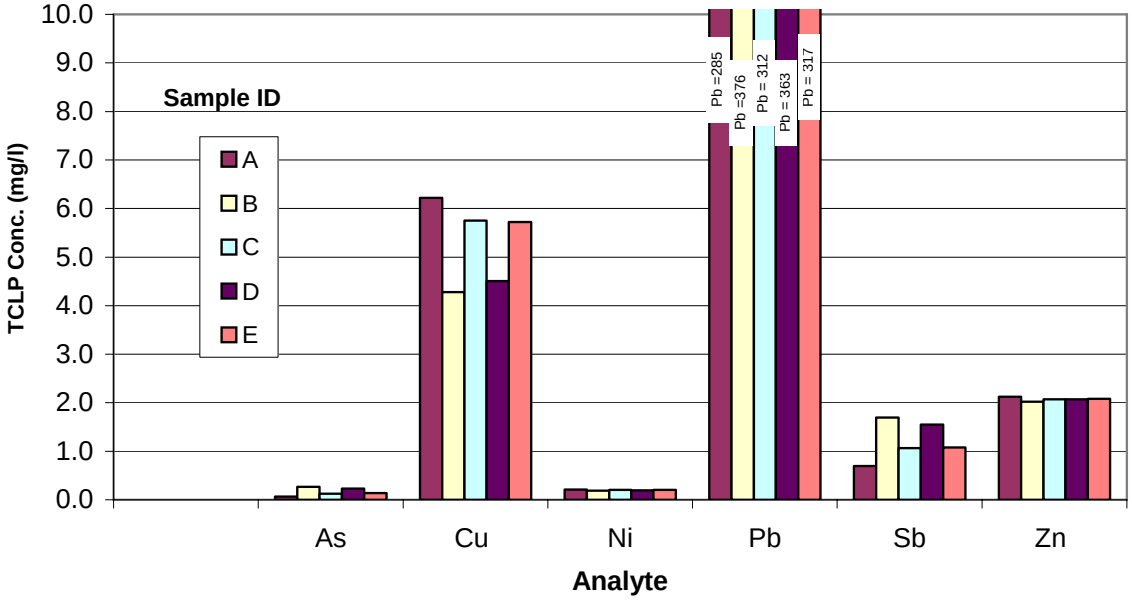


Figure 5-5. Baseline TCLP concentrations (scale 0 to 10 mg/L).

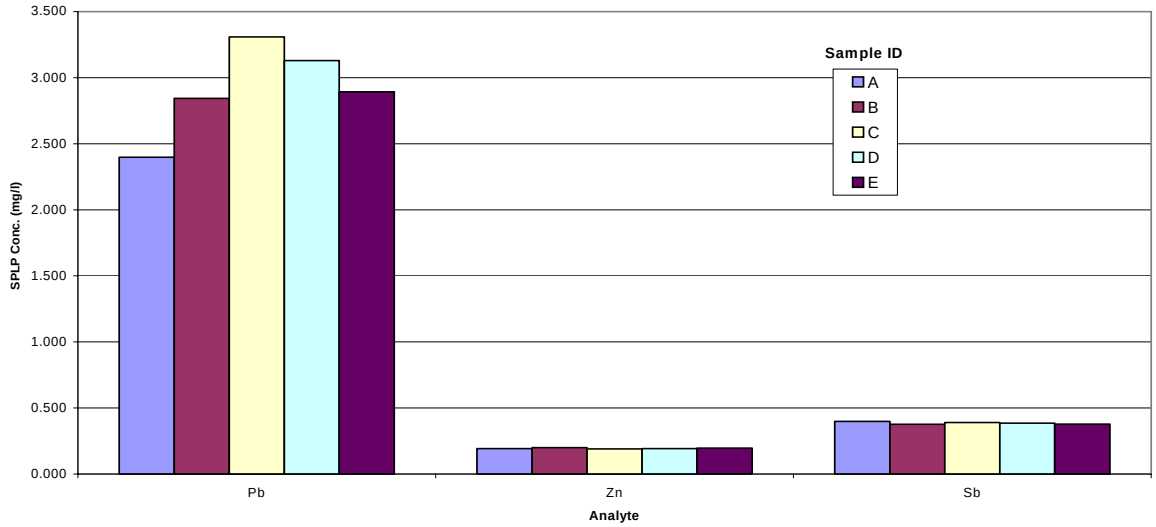


Figure 5-6. Baseline SPLP leachate concentrations.

5.2.2 Phosphate Concentration

Five soil samples were collected from the 5-gallon bucket of untreated soil for baseline phosphate concentration characterization. The baseline phosphate results are depicted in Figure 5-7. The average total phosphate concentration in the soil was 30.7 mg/kg (Table 5-3). The average free (leachable) phosphate and hydrolyzable phosphate concentrations were 2.46 mg/kg and 7.22 mg/kg, respectively, as shown in Table 5-3.

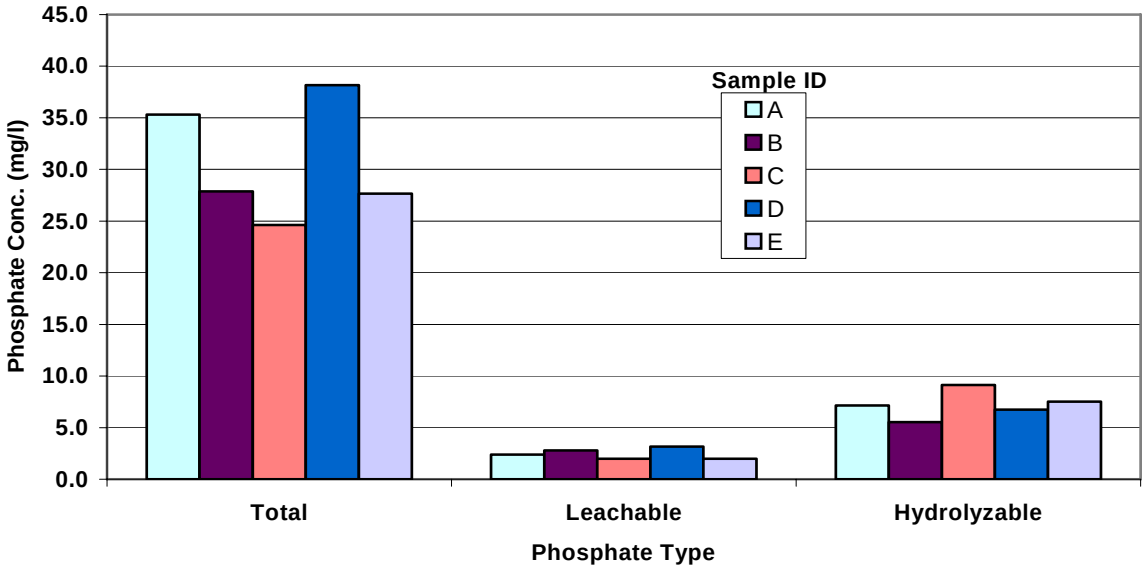


Figure 5-7. Baseline phosphate concentrations.

5.2.3 PBET

Four samples were collected from the 5-gallon bucket of untreated soil for baseline PBET analysis. These soil samples were extracted using a pH of 1.5 and four additional samples were extracted at a slightly higher pH of 2.3. As shown in Table 5-3 the average lead PBET concentration of the soil extracted at pH 1.5 is 61.7 mg/L. The average lead PBET concentration extracted at pH 2.3 is 57.1 mg/L. The lead leachate concentration results for each sample are presented in Figure 5-8.

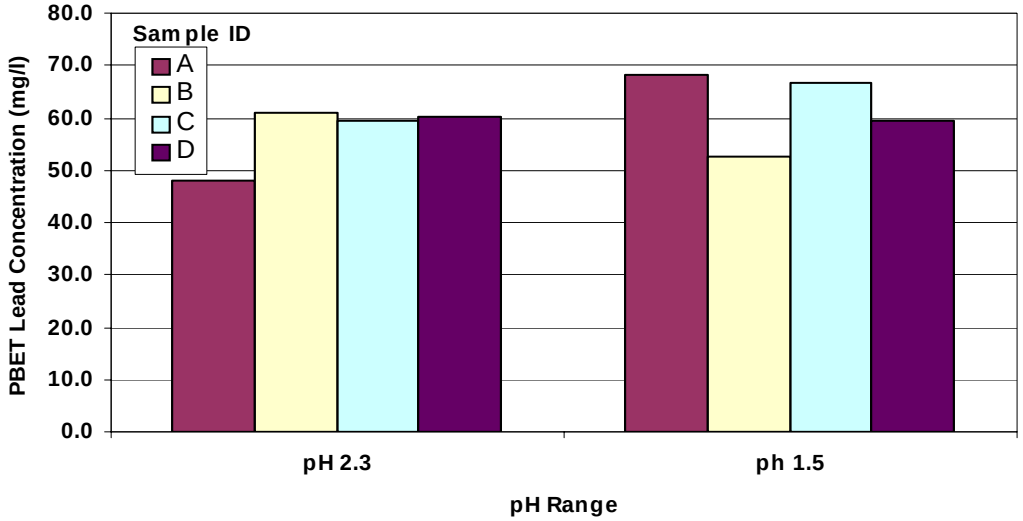


Figure 5-8. Baseline PBET lead concentrations.

5.2.4 MICROTOX®

Five baseline soil samples were subjected to the MICROTOX® soil toxicity screening test. These tests were conducted using the MICROTOX® system (International Standards Organization (ISO) 11348-3). As presented in Table 5-3, the average EC50 percent concentration of the five baseline analyses was 6.78 percent. The results of the baseline MICROTOX® analyses for each soil sample are presented in Figure 5-9. When compared to reference substances known to cause bacterial inhibition (30 ppm chromated copper arsenate (CCA) - wood preservative EC50 = 3.95 percent and 10 percent Isopropanol EC50 = 12.55%), the untreated soil was considered to be relatively toxic to the bacterial population used in the MICROTOX® toxicity test.

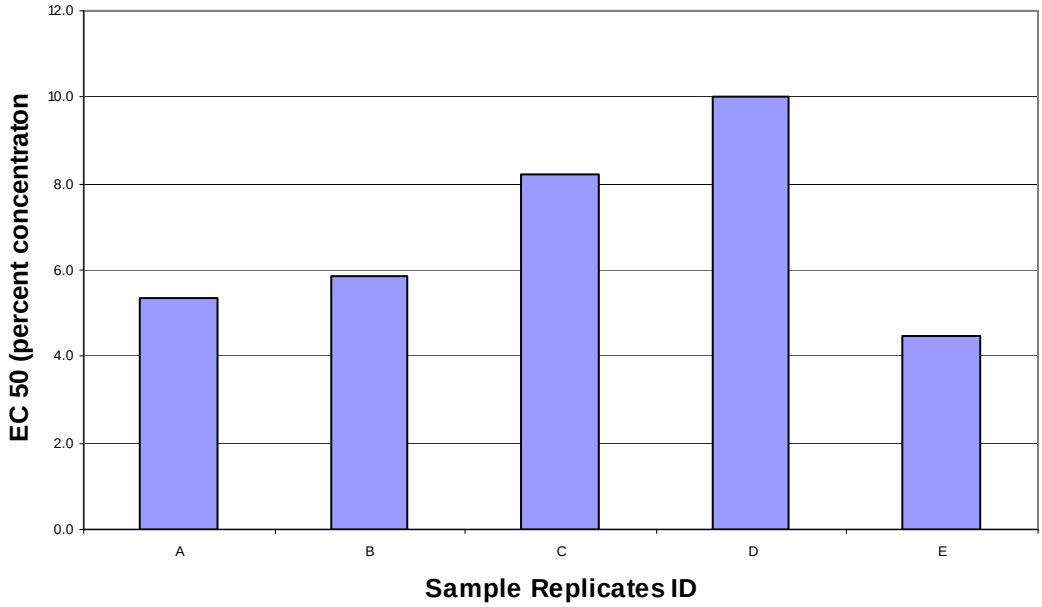


Figure 5-9. Baseline MICROTOX® data.

5.2.5 Physical Baseline Characterization

Typically five samples were collected from the representative 5-gallon bucket to conduct the physical tests. Soil samples were molded or prepared according to the appropriate test method and subjected to a total of 5 physical tests. For the CI test, six samples were subjected to baseline testing. The average results for four of the five tests (UCS, CI, Density, and Permeability) are presented in Table 5-4. The average results for the particle size analysis due to the nature of the test cannot be presented in table format and are presented in Figure 5-10.

For the UCS baseline data, a total of five molds containing three samples were compacted and subjected to UCS determination. The results of all 15 baseline UCS samples are presented in Figure 5-11. As shown in Table 5-4 the average UCS for the untreated soil was 16.8 psi. In addition the UCS analyses, each of these samples were subjected to the bulk density analysis prior to UCS testing. The baseline bulk density data for these 15 samples are presented in Figure 5-12. As shown in Table 5-4 the average bulk density was 1.61 g/cc. Cone penetrometer data for each sample are presented in Figure 5-13 with the average cone index value measured at 150 psi (Table 5-4). The baseline permeability data for each sample are presented in Figure 5-14. The average permeability value was 5.54×10^{-06} (Table 5-4). The average of the five sample's particle size is presented in Figure 5-10. Individual baseline particle curves for each sample are presented in Appendix C. As seen in this figure, the Camp Withycombe soil on average has a greater percentage of fines than large particles.

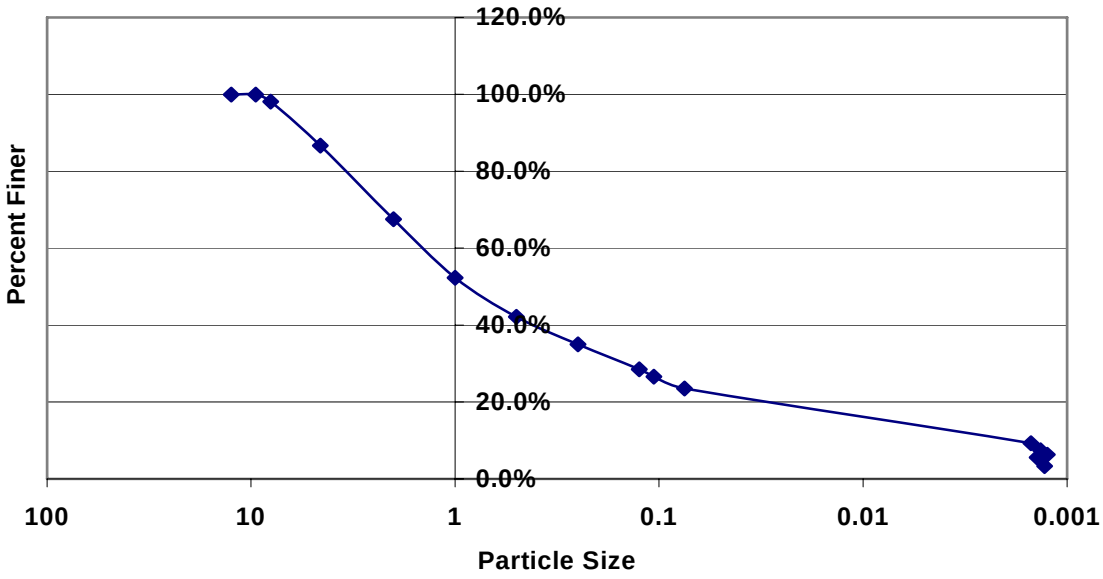


Figure 5-10. Particle size baseline data.

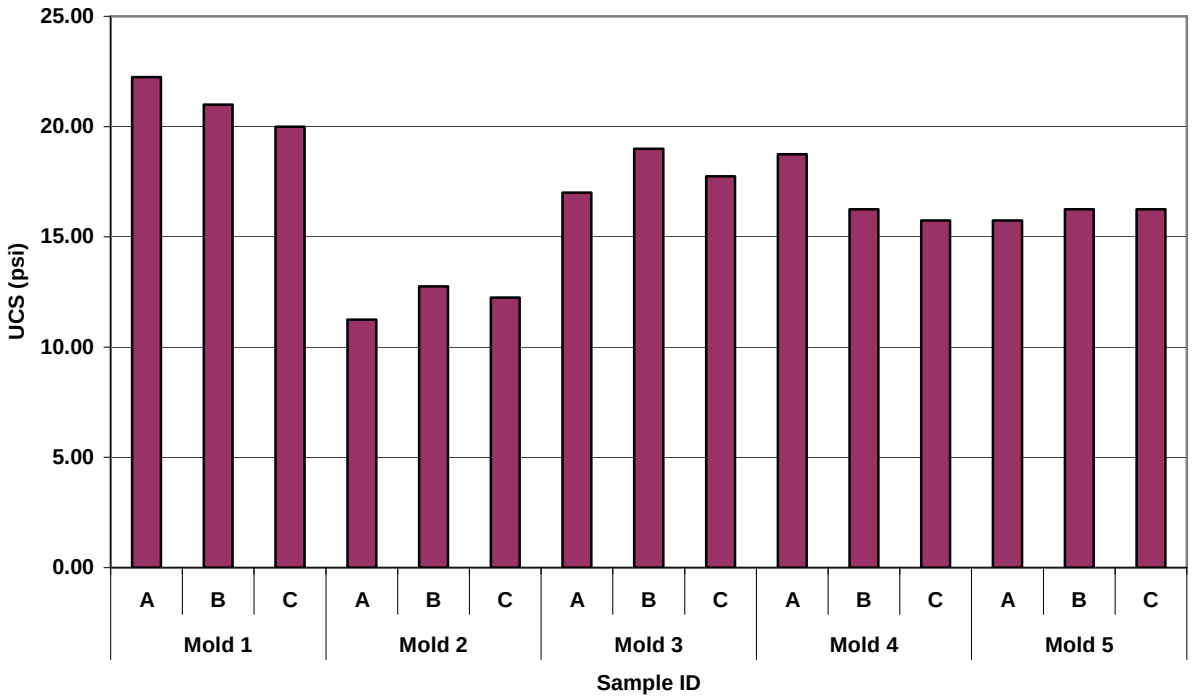


Figure 5-11. Baseline UCS data.

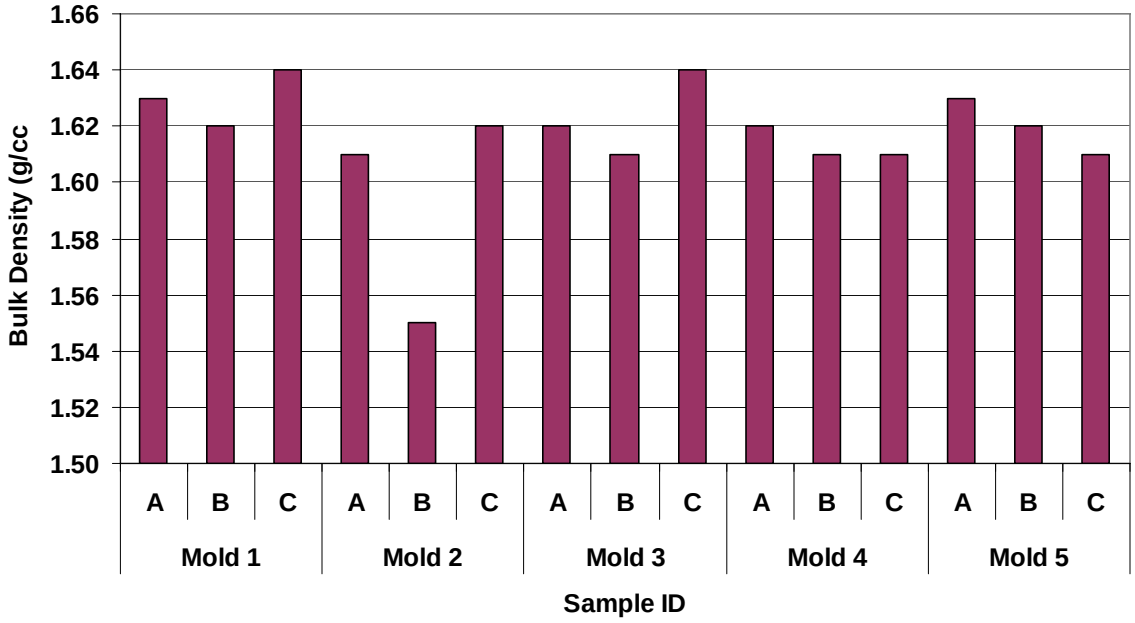


Figure 5-12. Baseline bulking data.

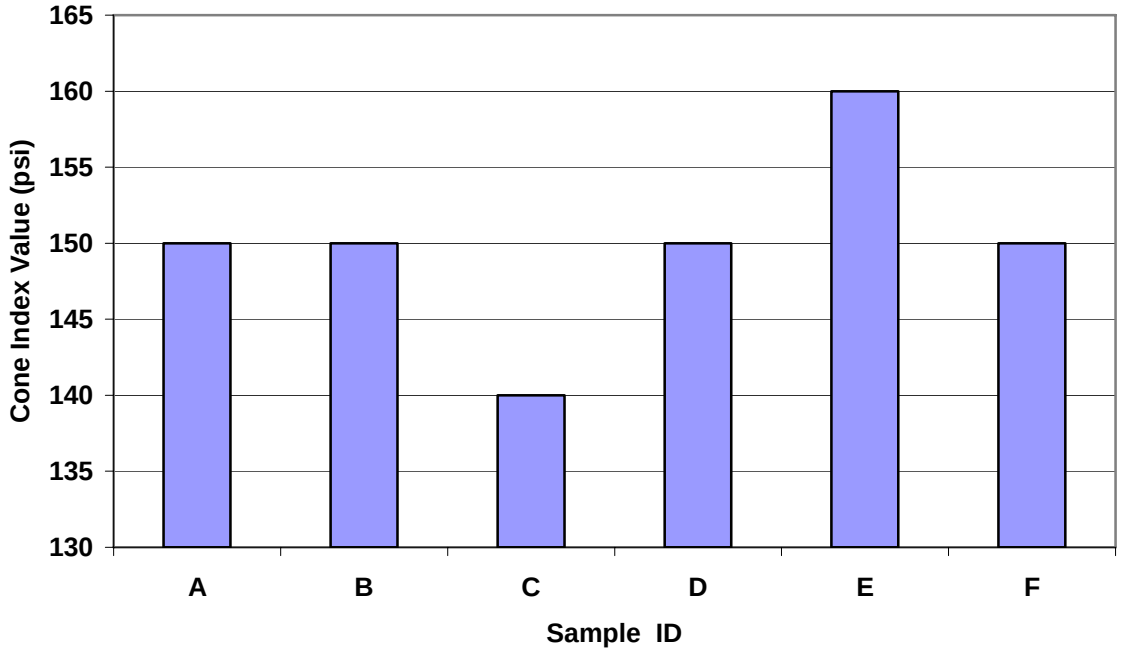


Figure 5-13. Baseline CI data.

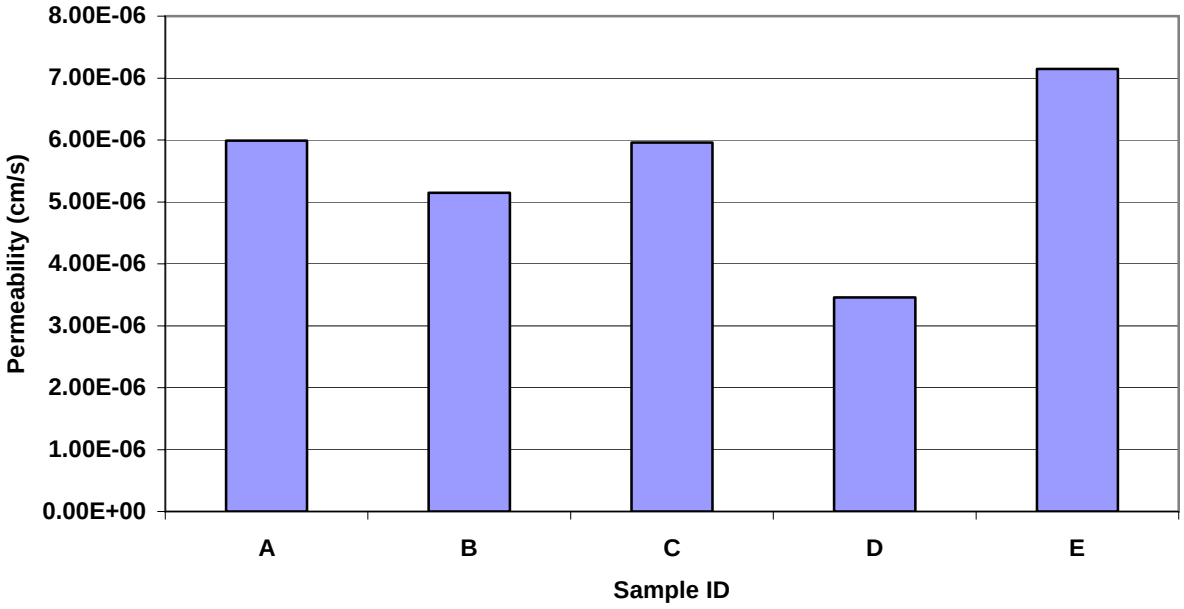


Figure 5-14. Baseline permeability.

6.0 GENERIC PHOSPHATE SCREENING RESULTS

The purpose of this generic or laboratory screening test was to identify the phosphate additive that minimizes soil lead and phosphate leaching while minimizing the additive to soil ratio. For this portion of the study seven different phosphate additives were combined with the Camp Withycombe range soil at five concentrations. These phosphate amended soils were compared to the baseline lead results. Phosphate was added at 1, 2, 4, 10, and 20 times the stoichiometric ratio (as phosphorus to lead). These laboratory screening tests only focused on lead contaminants in the soil. Results of these generic phosphate screening tests are given below.

6.1 Total Lead

Soil samples were subjected to seven generic treatment processes (listed in Table 4-4). The total lead concentrations for each treated sample (three replicates) were averaged separately and are presented in Figure 6-1. Because the soil was homogenized thoroughly and all samples for this portion of the study were collected from a single bucket of Camp Withycombe soil, in theory one would expect all samples to produce similar total lead results. As the phosphate additive was increased, a dilution of the soil lead concentration should have occurred because the additive contained very little lead. Thus, as the additive was increased, it was expected to lower the observed lead soil concentration. As shown in Figure 6-1, due to variances in the lead results this pattern was not observed. The average total lead content of these samples was 12,100 mg/kg and the standard deviation was 8,140 mg/kg. These results are similar to the baseline, which had a lead concentration of 11,700 mg/kg with a standard deviation of 5,126 mg/kg. The expected dilution effect was assumed to have been masked by the sample heterogeneities.

6.2 TCLP

Results of the average TCLP lead concentrations of the generic phosphate screening samples are shown in Figure 6-2. The data indicates that for all treatments, phosphate was effective at reducing the leachable lead concentration (a minimum 60 percent reduction) when compared to the untreated sample. As observed in Figure 6-2, phosphoric acid (H_3PO_4) was the most effective treatment for reducing TCLP lead leachate concentration. This was followed by hydroxyapatite. The general trend for the hydroxyapatite and H_3PO_4 samples was a decrease in TCLP lead leaching as additive concentration was increased. However, at the 2 times stoichiometric ratio for hydroxyapatite, the TCLP lead concentration was approximately 120 mg/L. This increase did not follow the typical data trend. It is believed that this increase was an anomaly probably resulting from lead particulate contained in the sample. Three replicate samples were analyzed for this treatment. TCLP lead leachate concentrations of 2.6, 6.5, and 348 mg/L were measured in the replicate samples. The elevated value of 348 is 76.5 times the average of the other samples. Excluding this anomaly yields a TCLP lead concentration of 4.6 mg/L for hydroxyapatite at 2 times stoichiometric ratio.

In general, samples treated at 4 times the stoichiometric ratio showed a substantial reduction in the TCLP leachate concentration. One exception was for bone ash, where the lead leachate concentration was 60 mg/L. At 4 times stoichiometric ratio, most samples pass TCLP resulting in <5 mg/L TCLP leachate concentration.

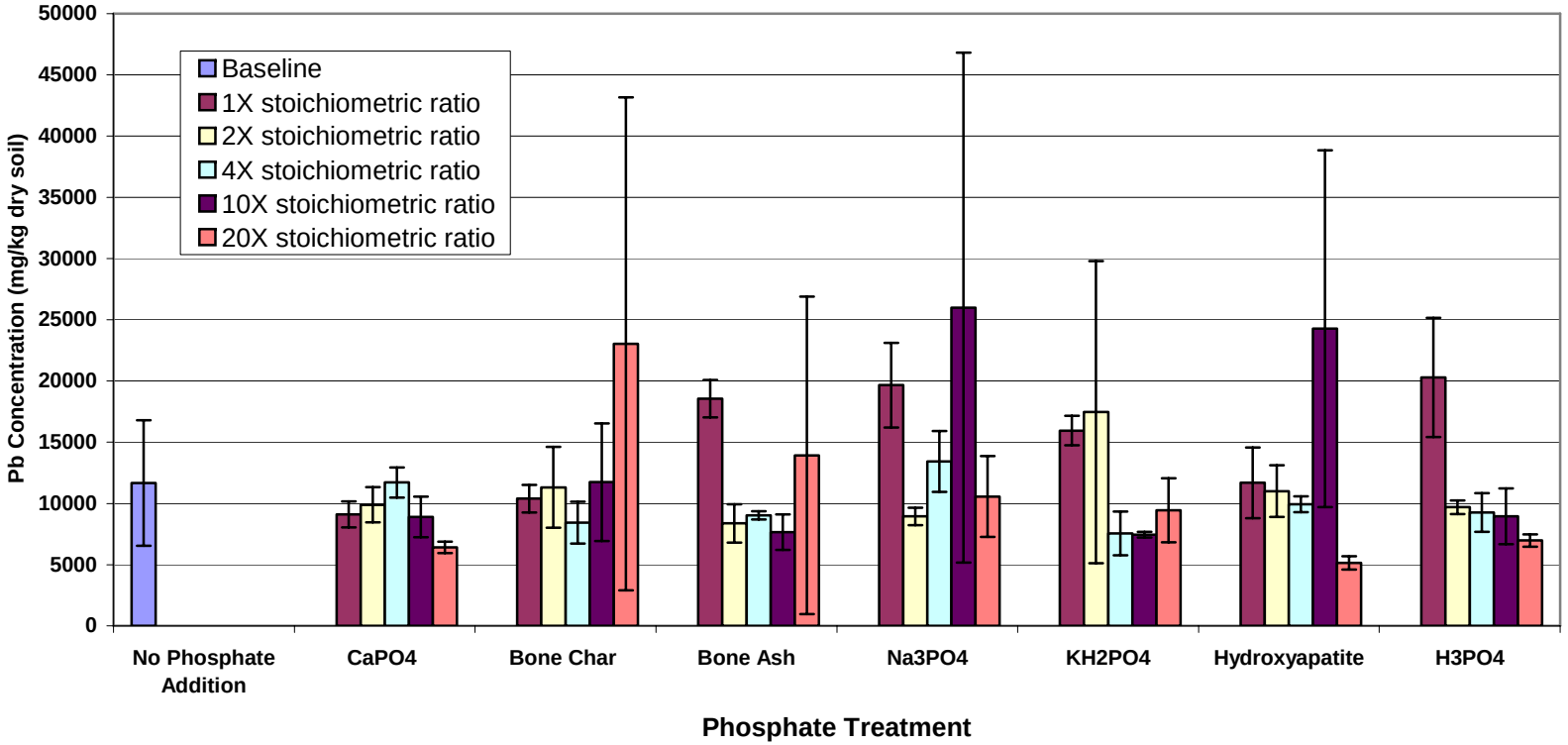


Figure 6-1. Total lead in generic phosphate screening samples.

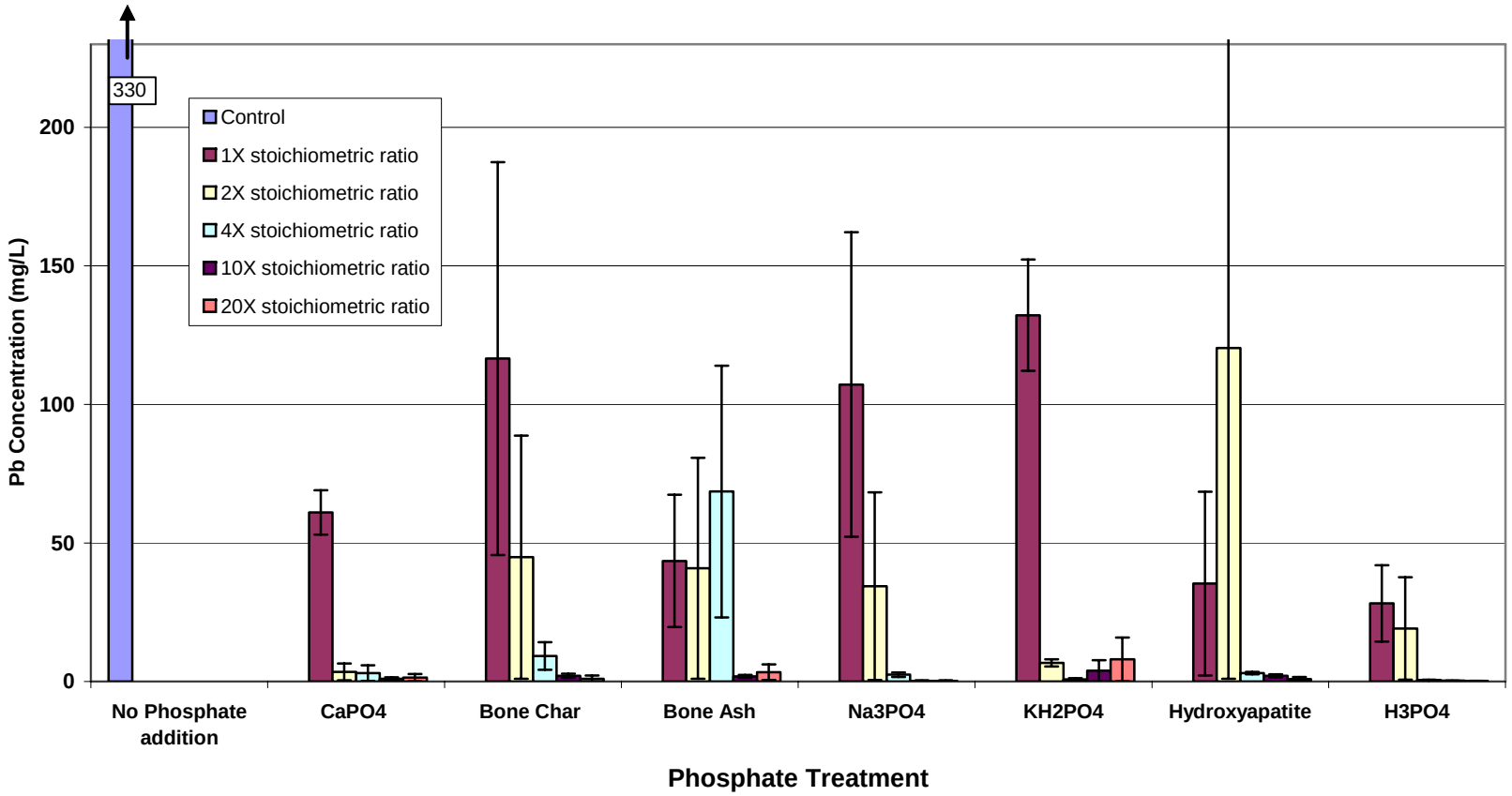


Figure 6-2. Generic phosphate screening average TCLP lead concentrations.

6.3 SPLP

Average results of the SPLP lead concentrations for the generic phosphate screening samples are shown in Figure 6-3. As seen in this figure, all forms of phosphate treatment were effective in reducing the lead SPLP lead leachate concentration. As observed for the TCLP, H_3PO_4 was the most effective at reducing the SPLP lead concentrations. Hydroxyapatite and sodium phosphate were also effective in reducing the SPLP concentrations. Many of the SPLP samples were also below the MDLs at higher phosphate concentrations. This indicates that these treatments were highly effective in reducing the SPLP leaching of lead. This was evident by a minimum reduction of 76 percent for all the phosphate additive ratios evaluated.

In general, samples treated at 2 times the stoichiometric ratio showed a substantial reduction in the SPLP lead concentration for all phosphate treatments. One exception was bone char, which showed a lead concentration of 0.34 mg/L. In general, it appears that most treatments were effective in reducing the SPLP lead leachate concentrations.

6.4 Phosphate

6.4.1 Total Phosphate

The average total phosphate results of the generic phosphate screening samples are presented in Figure 6-4. As the phosphate amount added to the samples increased, the total amount measured by the test increased as expected. While these results are not that enlightening, these results do indicate that the extraction method used to measure total phosphate was effective and will be useful in interpreting the vendor evaluation portion of the study.

6.4.2 Leachable Phosphate

Figure 6-5 presents the average leachable phosphate concentrations for each generic phosphate treatment screened. Based on the information presented in Figure 6-5, the most leachable forms of phosphate were phosphoric acid and Na_3PO_4. This was expected because these forms of phosphate are very soluble. Although these treatments had the greatest phosphate mobility, there was not a dramatic difference in the phosphate leachability when compared to the other five treatments. It was interesting to note that hydroxyapatite (a relatively insoluble phosphate form) had higher phosphate leachability than KH_2PO_4 (a highly soluble phosphate form). This was true at every stoichiometric ratio evaluated. This was not expected. The increased phosphate leachability may be the result of nitric acid being added to the soil in an attempt to solubilize the lead to increase the production of pyromorphite.

In general, phosphate leachability increased dramatically at 10 times the stoichiometric ratio of phosphate addition. This elevated phosphate leachability was not desired. Leachable phosphate in soil may result in high levels of phosphate in surface runoff which is regulated by the USEPA. When phosphate is applied under actual site conditions, the phosphate transport must be minimized to reduce potential environmental impact.

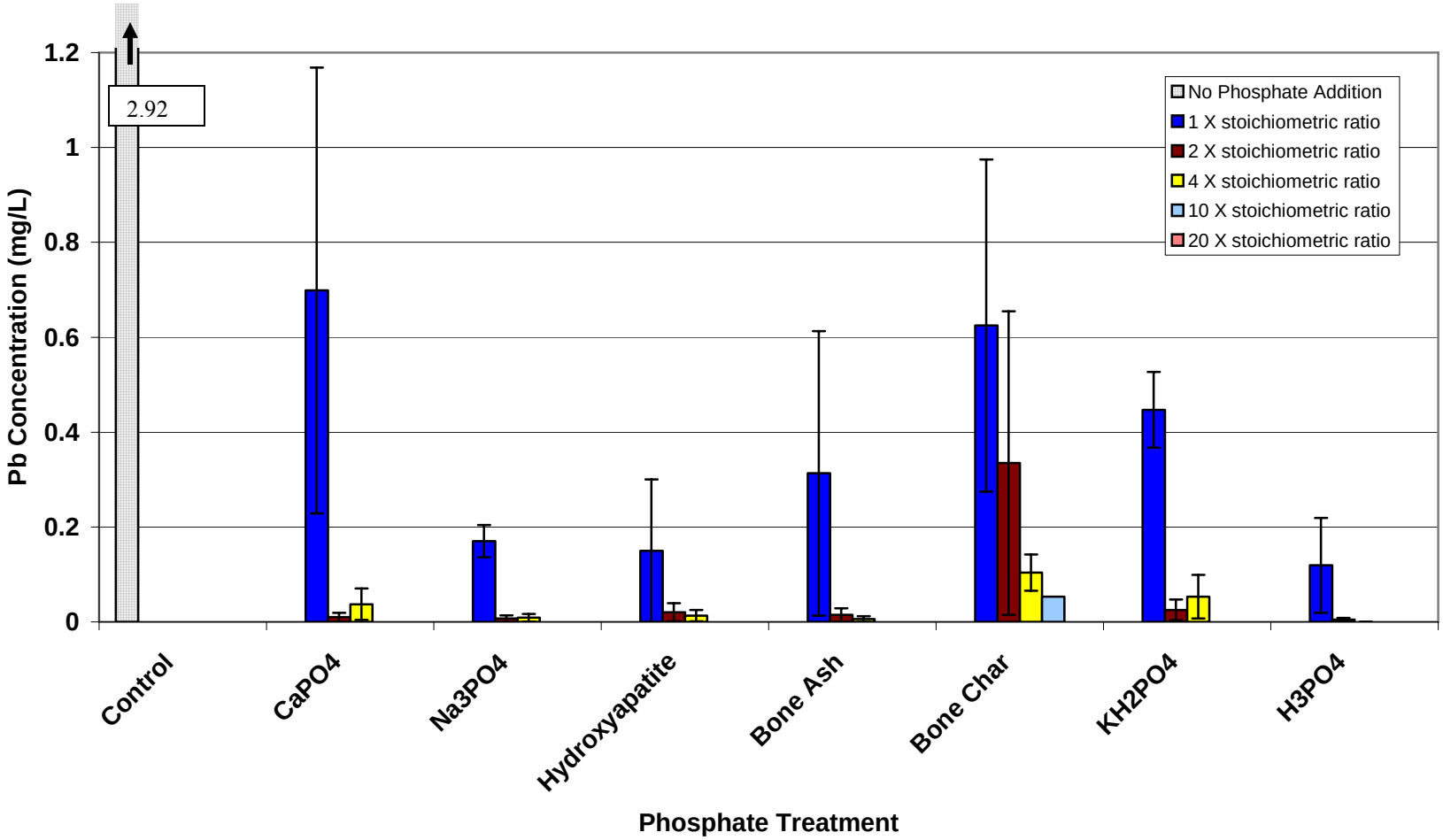


Figure 6-3. Generic phosphate screening average SPLP lead concentrations.

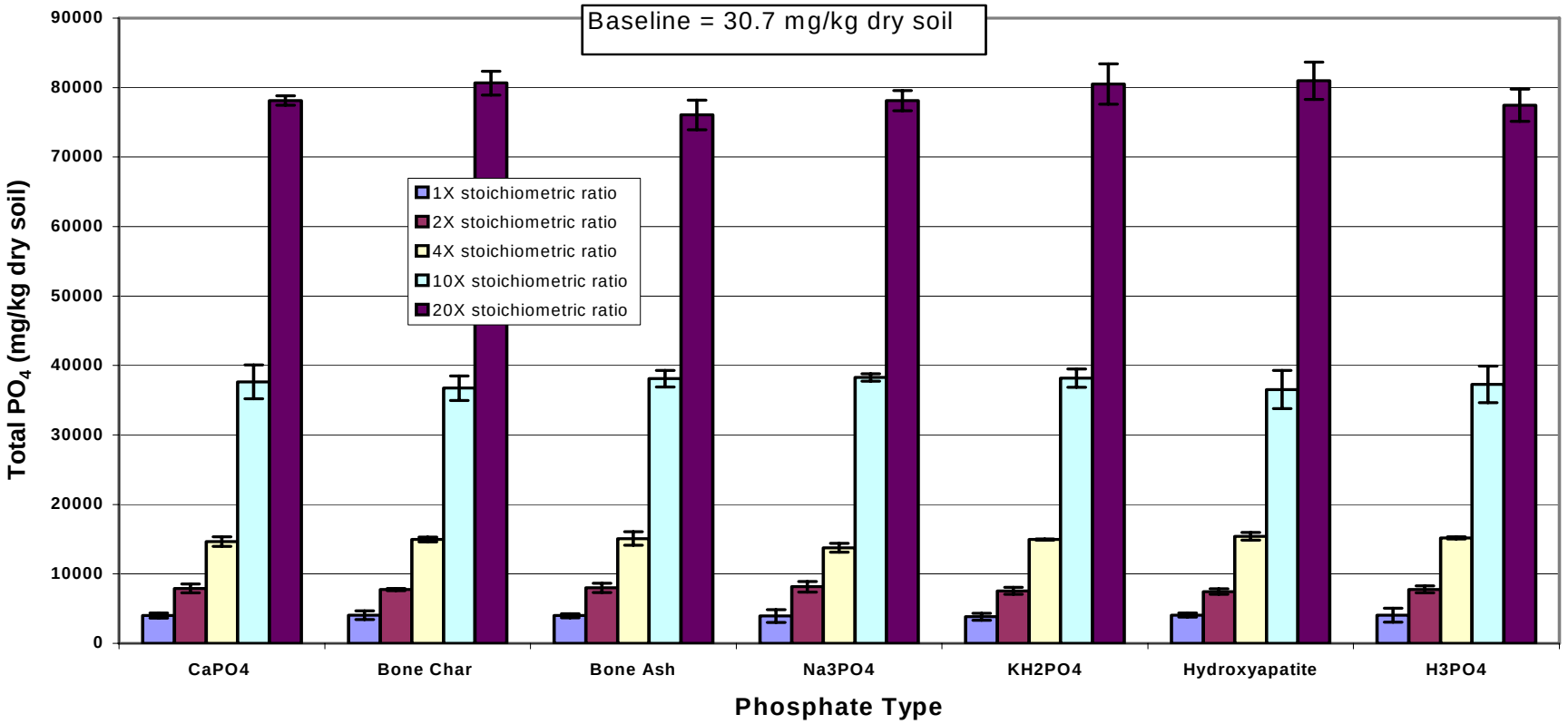


Figure 6-4. Generic phosphate screening average total phosphate (with acid amended soils).

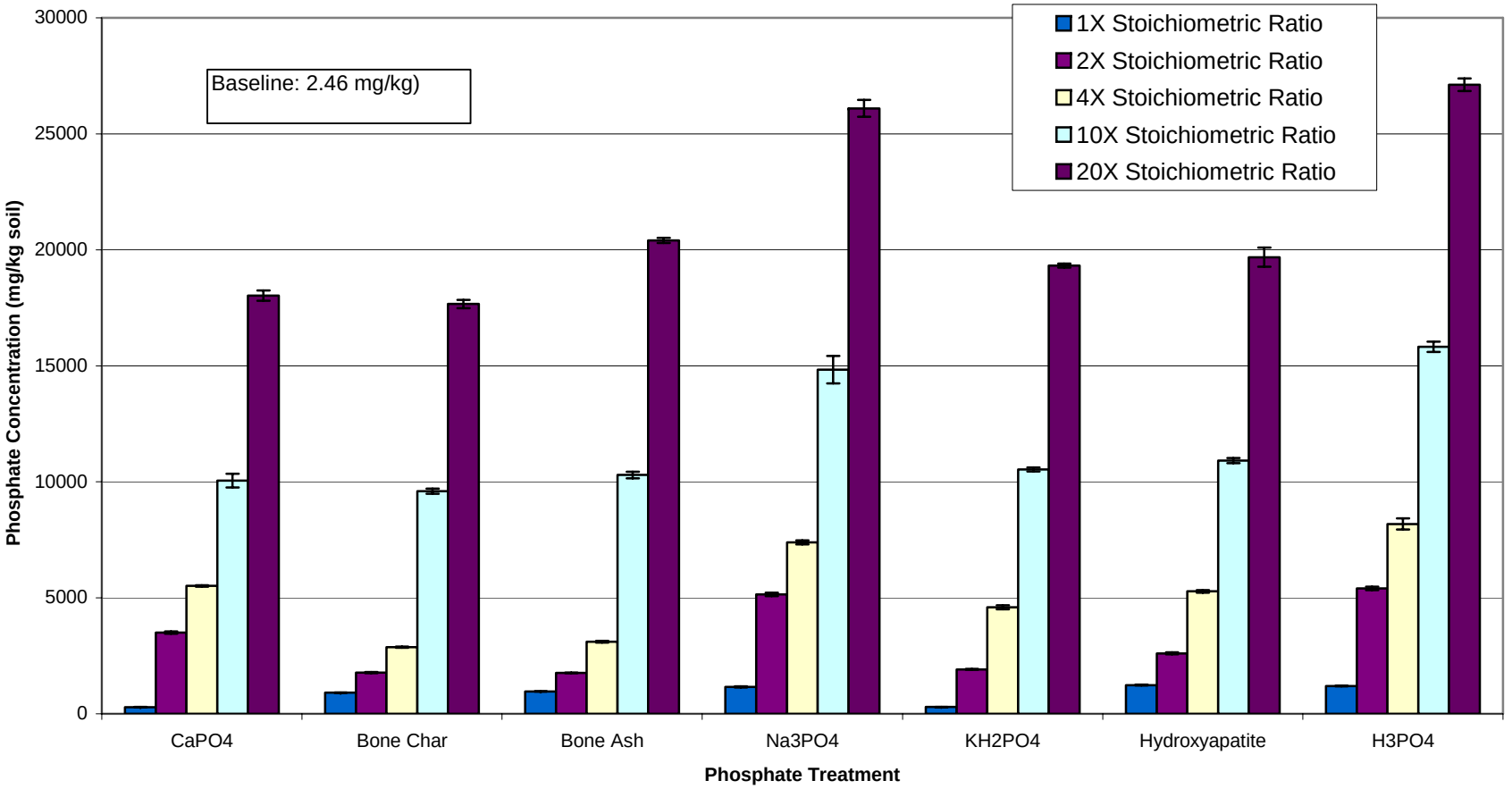


Figure 6-5. Generic phosphate screening average leachable phosphate (with acid amended soils).

6.4.3 Hydrolyzable Phosphate

The hydrolyzable test for phosphate measures the fraction of phosphate that is available as soluble phosphate but is complexed and not readily available for reaction. For this test, acid is added to the DI extract which breaks down the organic complex. This releases the phosphate for quantitation.

Figure 6-6 presents the average hydrolyzable phosphate concentration for the generic phosphate screening samples. The results presented in Figure 6-6 indicate that there was a large concentration of complexed phosphate. This increased with increasing phosphate addition. At 1 times the stoichiometric ratio, the sample with the highest amount of hydrolyzable phosphate was hydroxyapatite. This was surprising because the hydroxyapatite had a low solubility and there was less phosphate in the distilled water extract (leachable results Figure 6-5). At the higher levels of phosphate treatment, the samples with the most hydrolyzable phosphate concentrations were phosphoric acid and sodium phosphate.

6.5 Results of the Modified Laboratory Treatment

Initially acid was added to the soil samples to increase the solubility of the lead and phosphate amendments. Based on literature information, the lower pH was expected to enhance the immobilization of the lead contaminants. For this portion of the study acids were not added to the soil. This was conducted to decrease the excessive phosphate leachability which was observed in Figure 6-5. While a reduction in phosphate leachability was desired, it was anticipated that lead immobilization would also be impacted. It is postulated that both lead and phosphate must be in solution for pyromorphite formation. Testing was conducted to evaluate this hypothesis. These studies were conducted using only the optimal phosphate amendments at the optimal concentrations (4 times stoichiometric ratio of H_3PO_4, 4 times hydroxyapatite, and 4 times hydroxyapatite with acid additions for comparison purposes).

Figure 6-7 presents the average TCLP results of the modified phosphate screening samples. As indicated by Figure 6-7, these modifications were effective in lowering the lead concentrations to below USEPA regulatory levels. Figures 6-2 to 6-7 show similar lead TCLP concentrations. This indicates that the acidification of the soil had little effect on the phosphate-lead reaction for the TCLP. Both acidified and non-acidified soil had TCLP concentrations ranging from 0.6-1.2 mg/L.

Figure 6-8 presents the leachable phosphate results for the modified phosphate screening samples. The phosphate from the phosphoric acid treatment was able to leach into solution, but the hydroxyapatite solutions did not leach in extremely large quantities. Comparing Figure 6-5 to Figure 6-8, there was a reduction in the hydroxyapatite PO_4 leachability from 5000 to 400 mg PO_4/kg soil. This was expected due to the low solubility of hydroxyapatite. It appears that the nitric acid addition did little to effect the TCLP concentration, but substantially increased the phosphate leachability. The modified soil treatment method was successful in reducing the phosphate leachability of the soil, so soil acidification prior to phosphate treatment was eliminated from further study.

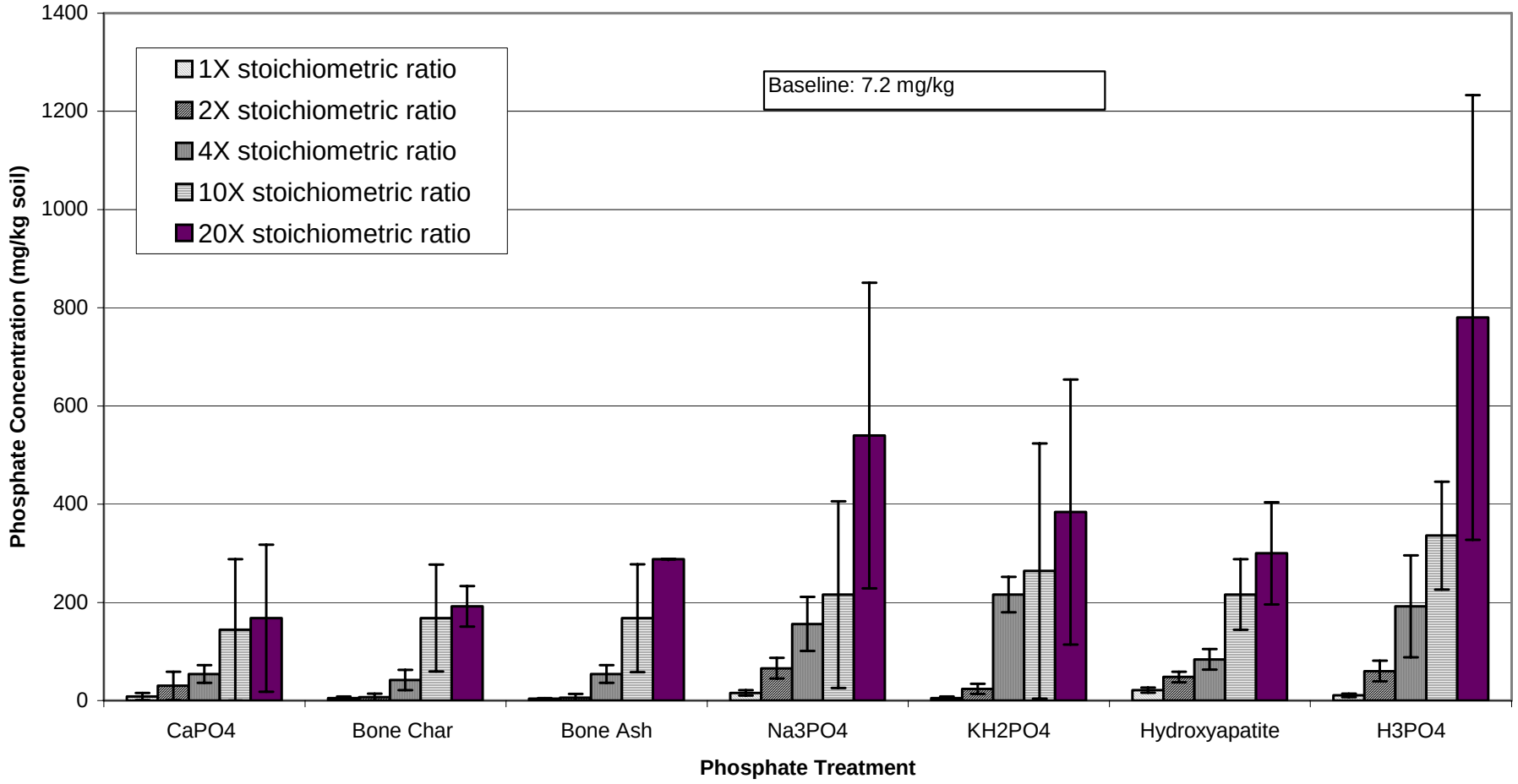


Figure 6-6. Generic phosphate screening average hydrolyzable phosphate (with acid amended soils).

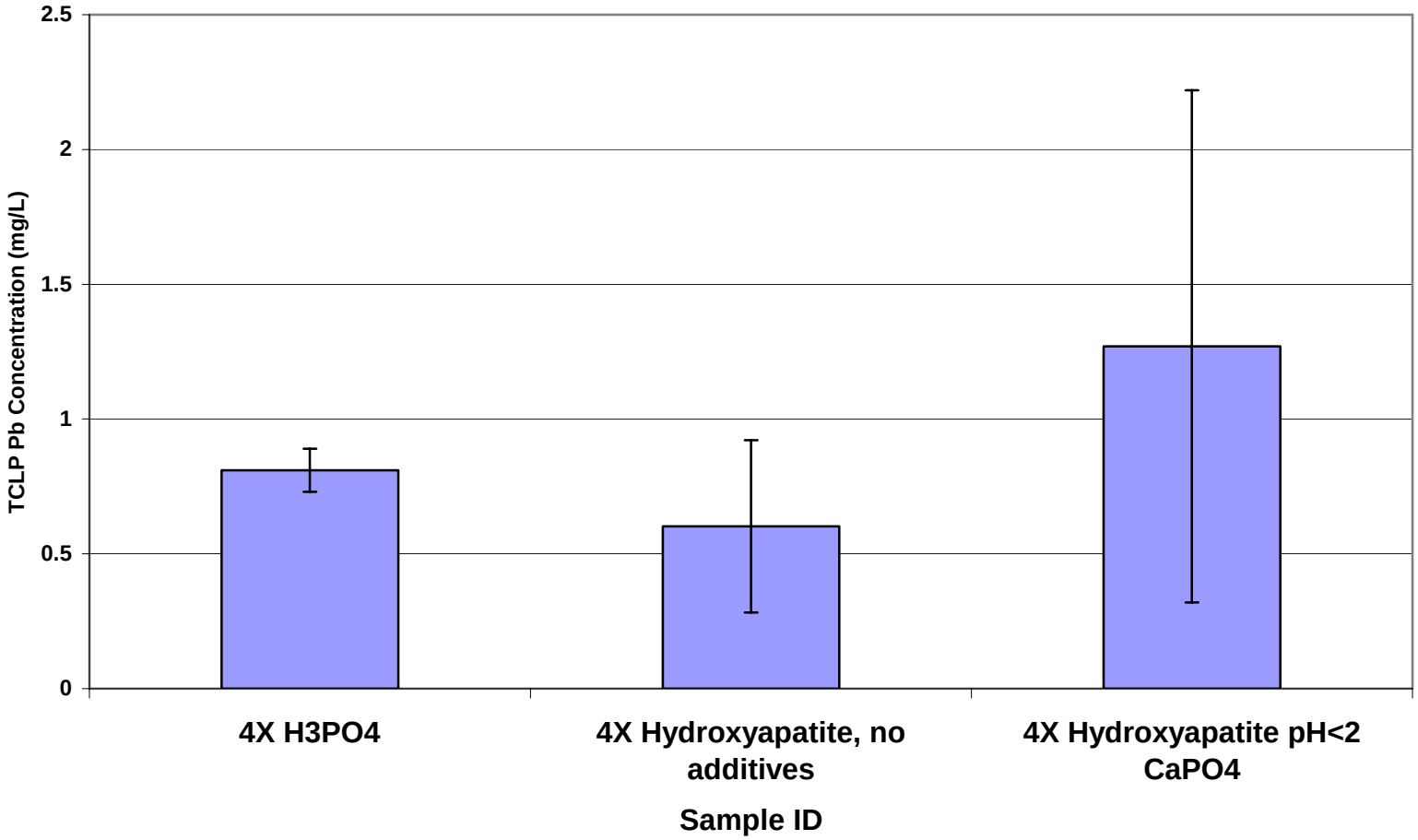


Figure 6-7. TCLP results of the modified generic samples.

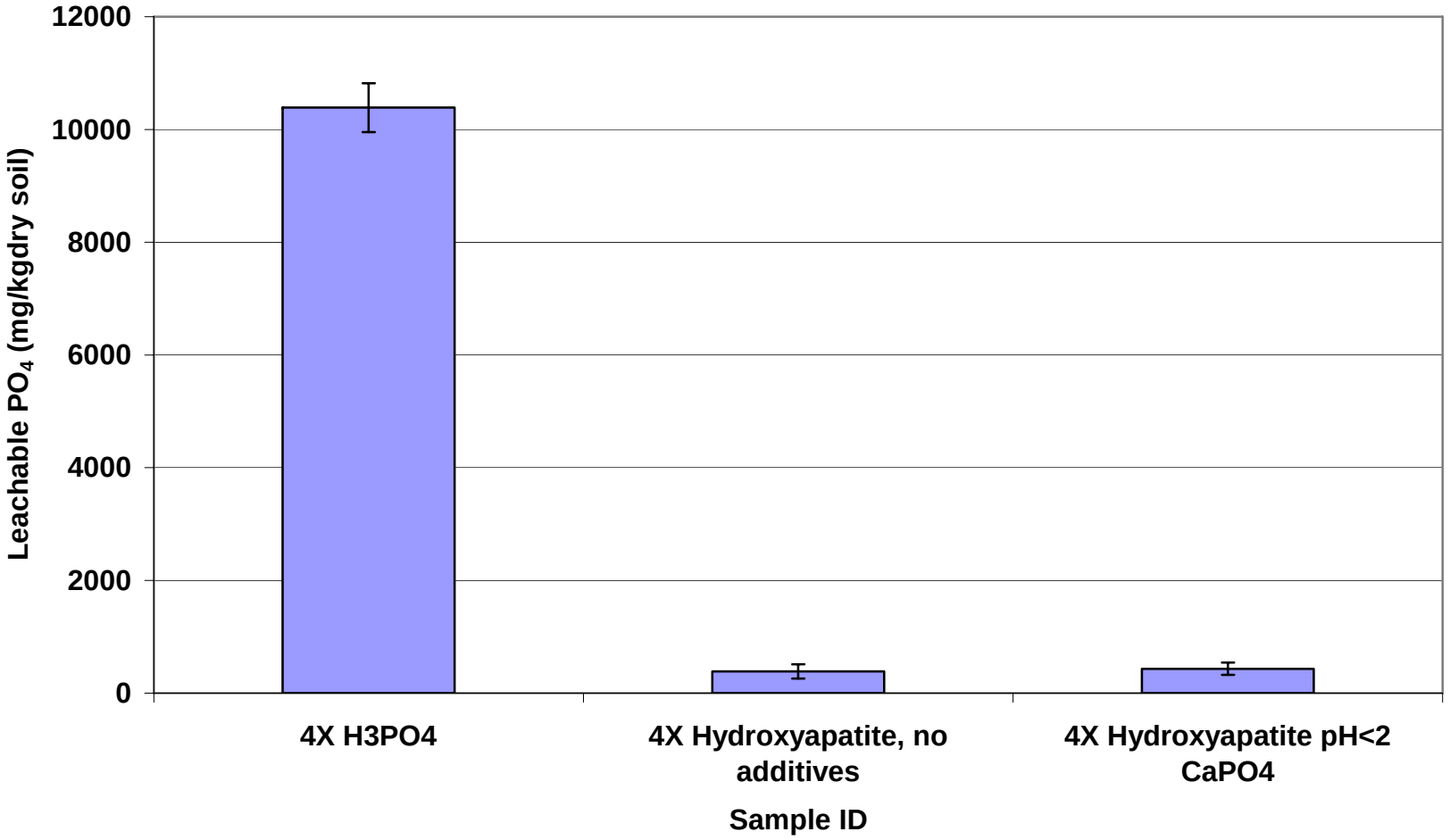


Figure 6-8. Leachable phosphate results of the modified generic samples.

6.6 Summary of Laboratory-Treated Samples

The results of all the generic phosphate screening tests indicated that the lead leachability decreased with increasing phosphate addition. Phosphoric acid was the most effective treatment in reducing the leachability of all of the generic phosphate treatments evaluated. Hydroxyapatite and calcium phosphate also significantly decreased the leachability of lead. The 4 times stoichiometric ratio was the concentration of phosphate additive where the soil to additive ratio was minimized, the phosphate leaching was minimized, and the lead mobility was minimized (TCLP <5 ppm). As expected, the phosphate forms that were more soluble (i.e. phosphoric acid and sodium phosphate) were most effective overall in reducing the leachability of lead. Unfortunately, these two forms of phosphate also produced the highest potential for phosphate leaching.

The phosphate type that was selected as the generic lab treatment was 4 times hydroxyapatite without soil pH adjustment. This phosphate form was selected because it lowered lead TCLP concentration and resulted in low phosphate leachability. The generic treatment conditions are given in Table 6-1.

TABLE 6-1. CONDITIONS FOR GENERIC TREATMENT

Phosphate Treatment	Hydroxyapatite
Concentration	4 times stoichiometric ratio
Amendments	No acid addition

7.0 RESULTS OF VENDOR TESTING

The results of the study are presented and discussed on an individual chemical and physical test basis. The chemical and physical tests conducted for this study were outlined in Figure 3-1 and described in Methods and Materials. Each of the vendor treatment sample and the generic lab treatment sample results are compared to the control sample results. The seven metal contaminants of concern (COC) identified during the baseline analyses discussed in section 4 were analyzed throughout all tests conducted with the exception of the PBET and plant analysis test. These two tests were only analyzed for lead.

Due to the fact that the lead is the major soil contaminant typically identified at small arms training ranges and that it is the COC with the highest concentration, the discussion of the results will focus primarily on lead contamination. The remaining six metals (arsenic, chromium, copper, nickel, antimony, and zinc) will also be discussed (in this order) with less emphasis. Whenever the chemical result for the COC was below the MDL, no result is presented. The results of these tests are described below.

7.1 Chemical Test Results

7.1.1 Total Digestions Results

Results of the total digestions on all of the vendor-treated samples for soil lead concentrations are presented in Figure 7-1. This data was normalized by taking the liquid digestate lead concentration in mg/L, multiplying by the dilution (typically 100 ml) and dividing this product by the dry raw soil mass (mg/kg dry raw soil) in the sample. This provided a direct method to correct for the dilution of the lead by the vendor additive as a result of treatment.

As seen in Figure 7-1, the concentration of lead extracted in the total digestion varied from an average high of 39,700 mg/kg to a low of 8,290 mg/kg. The value of 39,700 was beyond the criteria of 3 times the standard deviation and was considered to be an anomaly. Once this value was removed, the normalized soil lead concentrations were comparable to the baseline samples (Table 5-1) where the average soil lead concentration was 11,700 mg/kg dry wt.

Similar graphs are presented in Appendix D for the other COC (arsenic, chromium, copper, nickel, antimony, and zinc). The normalized soil COC concentrations were generally comparable to the baseline samples averages (Table 5-1). Figure 7-2 presents a log plot of the average concentration of each COC for each vendor treatment. The hierarchy of COC contained in the Camp Withycombe soil was as follows:

$$Pb >> Cu > Zn >> Ni > Cr > Sb > As$$

Table 7-1 presents the overall average (averaged over the replicates, sample age, and vendor treatment) for COC. The hierarchy of COC contained in the soil presented above is also seen using this table.

An analysis of variance (ANOVA) [using missing data (a generalized linear model (GLM) procedure)] was conducted using four classes as presented in Table 7-2 (COC = 7 levels, treatment = 6 levels, sample age = 6 levels, and replicates = 3 levels). This GLM analysis indicates at the 99.9 percent confidence level (CL) there is statistical evidence that the metals within the COC class are different, but there was no statistical evidence that there were differences between the Treatment, Sample Age, or Replicates classes. This was expected since the soil was homogenized prior to testing and justifies averaging the data.

TABLE 7-1. NORMALIZED SOIL CONCENTRATION FOR THE COC

COC	Normalized Concentration, mg/kg Dry Raw Soil
Arsenic	8.1
Chromium	27.6
Copper	988.3
Nickel	38.8
Lead	12830.5
Antimony	10.5
Zinc	206.7

COC = Contaminant of concern.

TABLE 7-2. CLASSES AND LEVELS USED IN THE ANOVA

Class	Levels[a]	Values
Contaminant of Concern	7	Arsenic, Chromium, Copper Nickel Lead Antimony, Zinc
Vendor Treatment	6	Control, Forrester, Lab, MT[2] RMT, Shaw
Sample Age	6	0, 14, 28, 60, 120, 360
Replicate	3	A, B, C

[a]Levels may change dependent upon available data (e.g. number of levels will be reduced if a COC is < MDL).

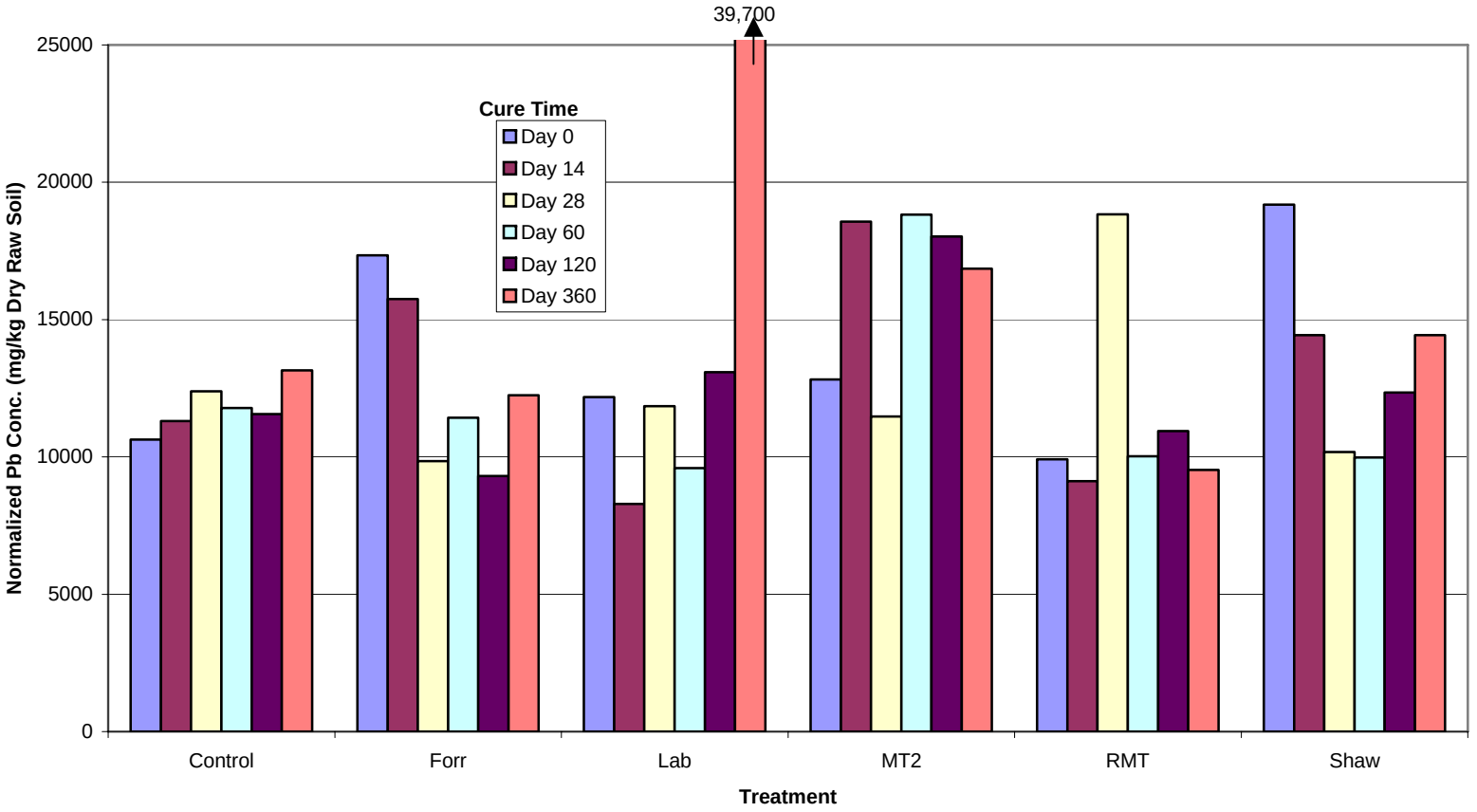


Figure 7-1. Normalized soil lead concentrations.

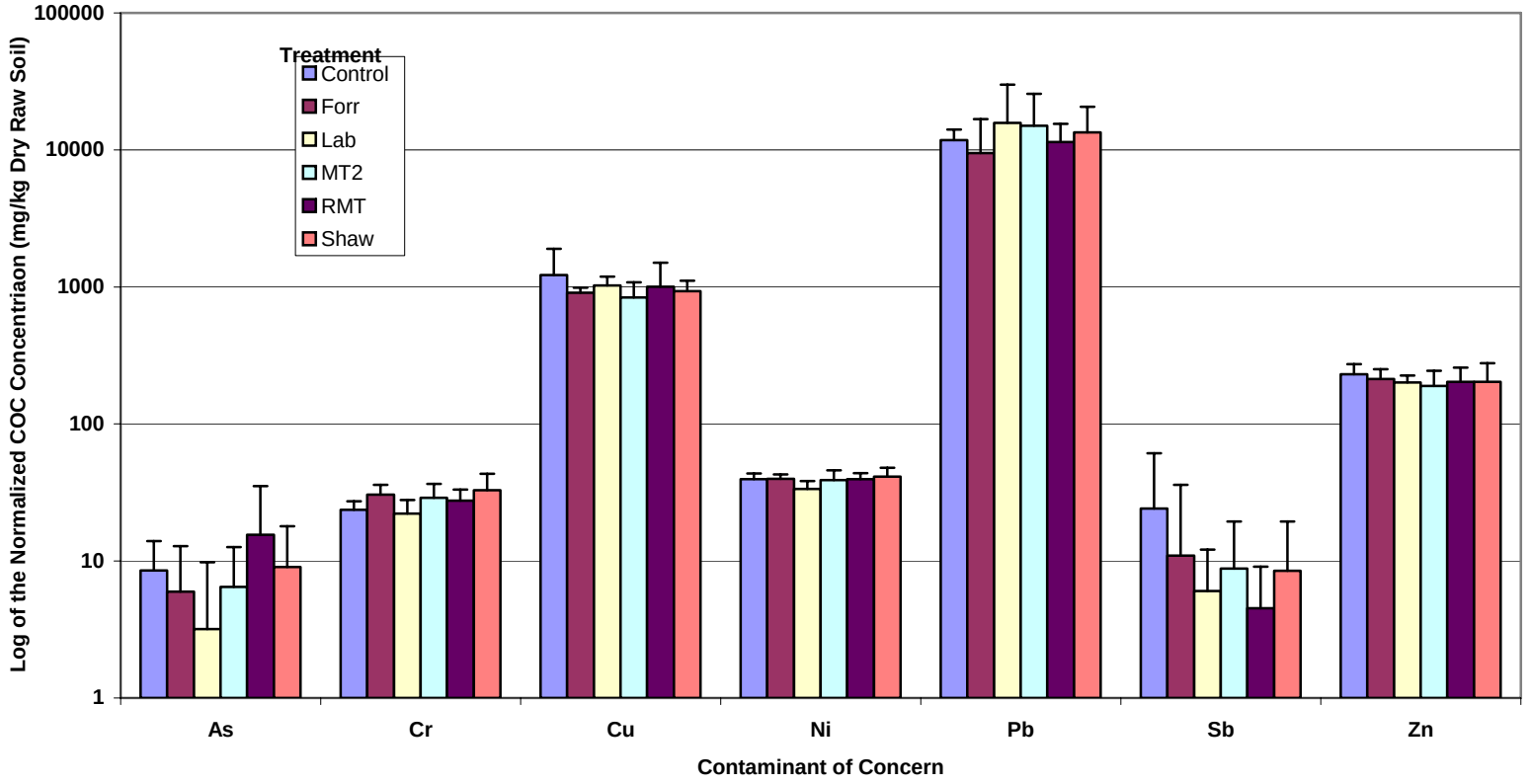


Figure 7-2. Average normalized soil concentrations for all COCs.

7.1.2 DI Leach

The purpose of the DI leach was to produce an extract to determine the phosphate mobility. In addition, the DI leach extract from each sample was subjected to metals analysis. The COC analysis of the DI leach extracts provided an indication of the mobility of the metals under non-aggressive extraction conditions (similar to normal precipitation conditions). The lead leachate concentration data are presented for each vendor and control sample with respect to sample age (3 data points per sample age) in Figure 7-3. The lead concentration results show that there was distinct grouping for the data. The control samples on average leached 5.8 mg/L, MT^2 samples on average leached 2.3 mg/L, and RMT samples on average leached 0.43 mg/L. The remaining vendors (Forrester, Lab, and Shaw) leached very little lead in the DI leachate when compared to the control and the MT^2 and RMT treated samples. These data indicate that lead was leachable from the untreated soil samples but much less leachable from the treated soils.

According to the USEPA the action level for treatment if lead is detected in drinking water is 0.015 mg/L (USEPA 2002). As observed in Figure 7-3, if the water exposed to the treated soils was used as a drinking water source, all samples would require treatment.

For easier comparison between the different vendor treatments the DI leach lead data were normalized to the dry raw soils concentration (mg/kg dry raw soil), and the results were averaged by replicate in Figure 7-4. These data show that the Forrester, RMT, and Shaw vendors were most efficient in immobilizing the lead.

The average DI leachate results for each COC are presented in Figure 7-5. These data average the sample replicate and age data for each COC and vendor/control. This figure indicates that lead is the most mobile COC, followed by copper and antimony. Such results are expected due to the higher levels of lead and copper found in the untreated soil as well as the relatively higher mobility characteristics of antimony with respect to the other COCs. Graphs showing the DI leachate data for each COC are presented in Appendix E.

A statistical ANOVA was conducted for this data set using four classes as presented in Table 7-2 (COC = 6 levels, treatment = 6 levels, sample age = 6 levels, and replicates = 3 levels). This analysis shows that there is statistical evidence to indicate that the COC and treatment are different, but there is no evidence to indicate that there is a difference between the different samples' ages or replicates. This analysis validates that the averaging of the data as presented in Figure 7-5 is a good approach to compare the results. To better understand the data, the normalized data for each vendor and COC were compared to their appropriate control samples to calculate a percent of the COC immobilized due to treatment. Equation [7.1] was used to calculate the percent of immobilized contaminant.

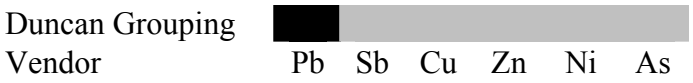
Using the Forrester lead concentration data for example:

$$\frac{\text{(Average Control Pb Concentration)} - \text{(Average Forrester Pb Concentration)}}{\text{(Average Control Pb Concentration)}} \times 100 \quad [7.1]$$

The percent of COCs immobilized by each vendor treatment is provided in Figure 7-6. This graph indicates that most COCs in the soils treated by the vendors were immobilized to some degree. The data indicates that lead, arsenic, nickel, zinc, and copper experienced significant immobilization. Antimony appeared to be the least affected by the treatment processes with only 2.5 to 49.3 percent of the antimony being immobilized.

The results of the Duncan multiple range tests indicated that the data was grouped as follows:

For the COC,



For the vendor treatment of lead:

Where the bars indicate the sample grouping.

The results of the Duncan tests indicated that the untreated samples leached statistically higher concentrations of lead than the treated samples and that little difference could be established between the Lab, Forrester, RMT, or Shaw treatments. In addition, antimony, copper, zinc, nickel, and arsenic were not statistically different in the concentration of each COC leached by the DI test.

7.1.3 TCLP

The TCLP lead concentration results were significantly affected by the addition of the various vendor treatments (Figure 7-7). The lead TCLP leachate concentrations (presented as leachate concentration in mg/L) for the control samples (Figure 7-7) were variable over the 0 to 360 day testing periods. Even with this variability the TCLP lead concentration results for the vendor-treated soil show a substantial reduction in TCLP lead concentration when compared to the control.

Averaging the control TCLP lead concentration results by sample age and replicate gives an average control TCLP lead concentration of 318 mg/L. All-vendor treated samples for lead TCLP results were below 5.0 mg/L TCLP criteria except for the 120- and 360-day Lab-treated samples, one 120-day RMT-treated sample, and one 60-day and all 120-day MT^2- treated samples. Based on the initial treatment results (0-day), all vendor-treated samples would have been classified as non-hazardous waste. However, most of the vendor treatment TCLP results indicated a trend towards increasing TCLP lead concentrations as the treated samples aged.

The ANOVA for the complete TCLP data set using four classes as presented in Table 7-2 (except COC = 6 levels) indicated that at a 99.9 percent CL only the COC and treatments have statistically significant differences (time and replicates were assumed to be the same). As explained in section 7.1.2, this analysis supported averaging the data over replicate and sample age. The TCLP COC concentration results are presented in Figure 7-8 for the control and each vendor treatment using this averaging method.

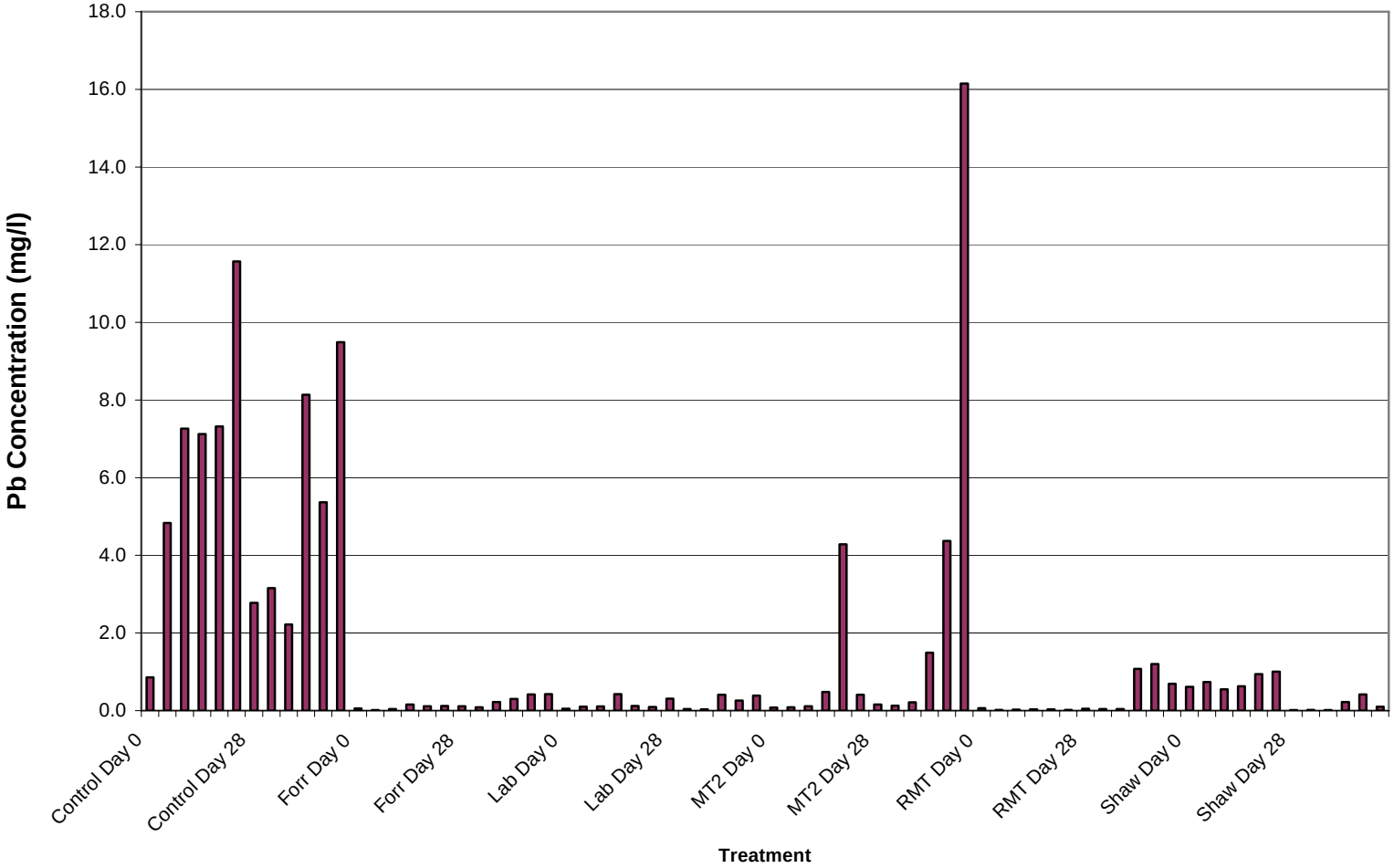


Figure 7-3. DI leach lead concentration results.

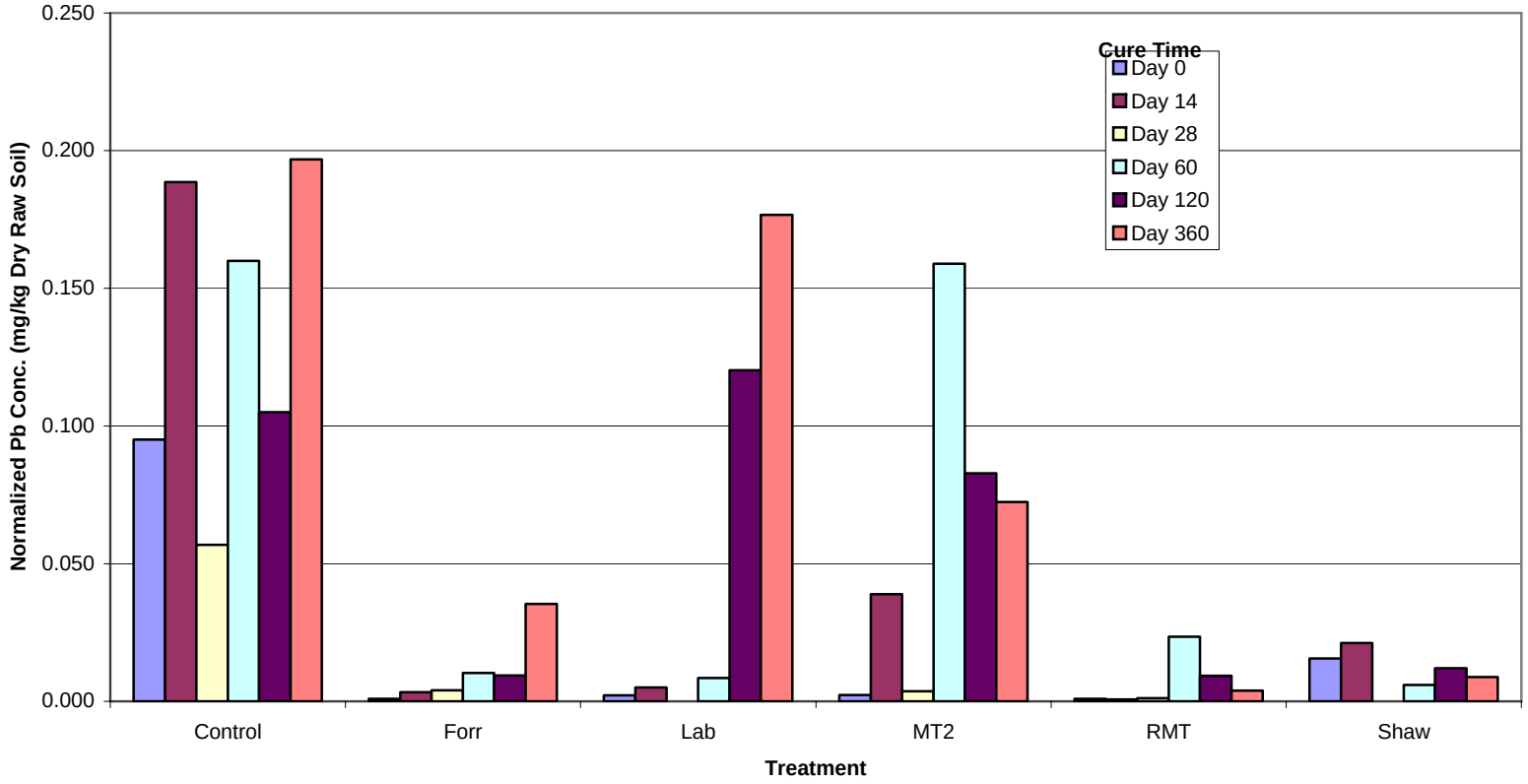


Figure 7-4. Normalized DI leach lead concentration results.

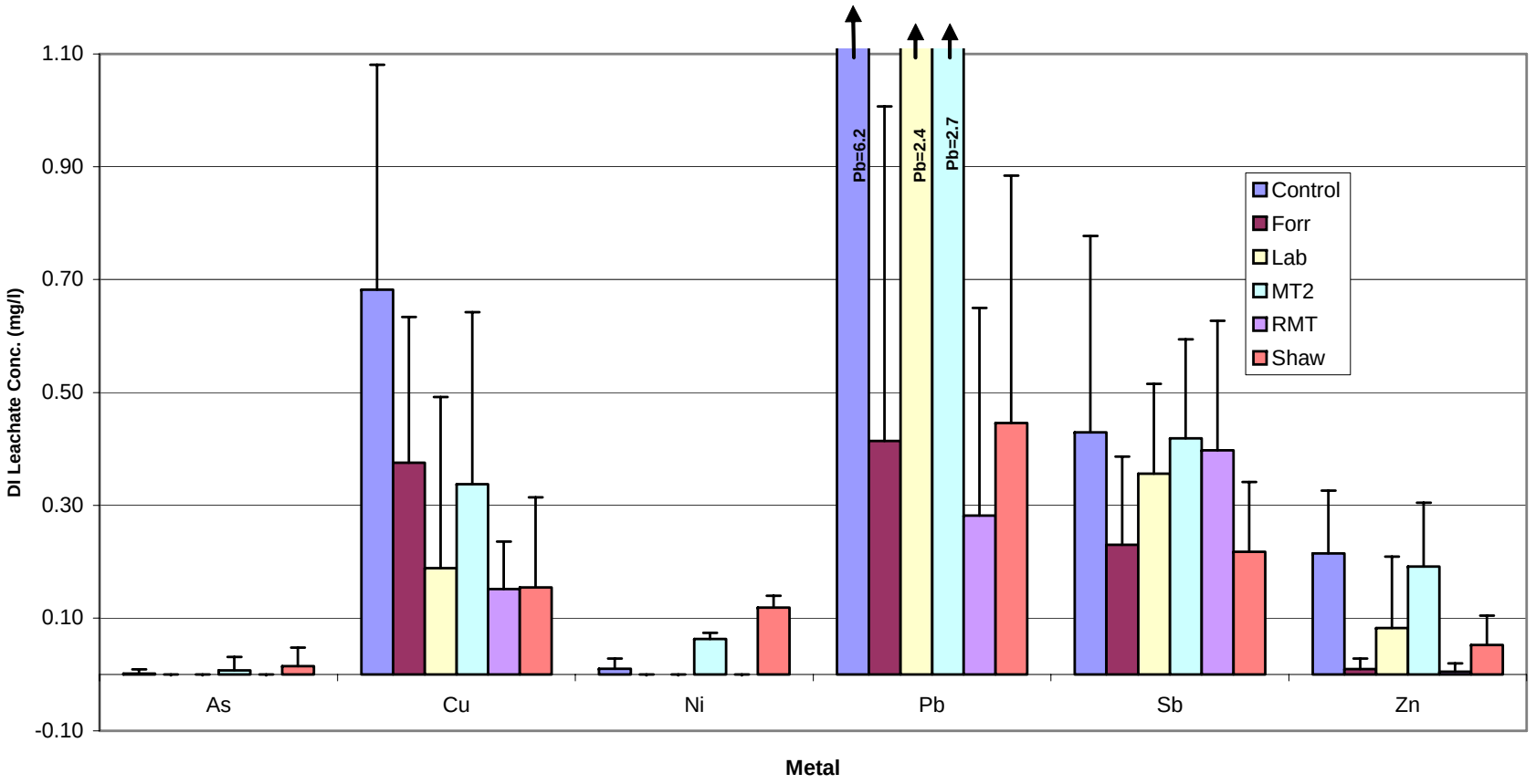


Figure 7-5. DI Leach COC concentration results.

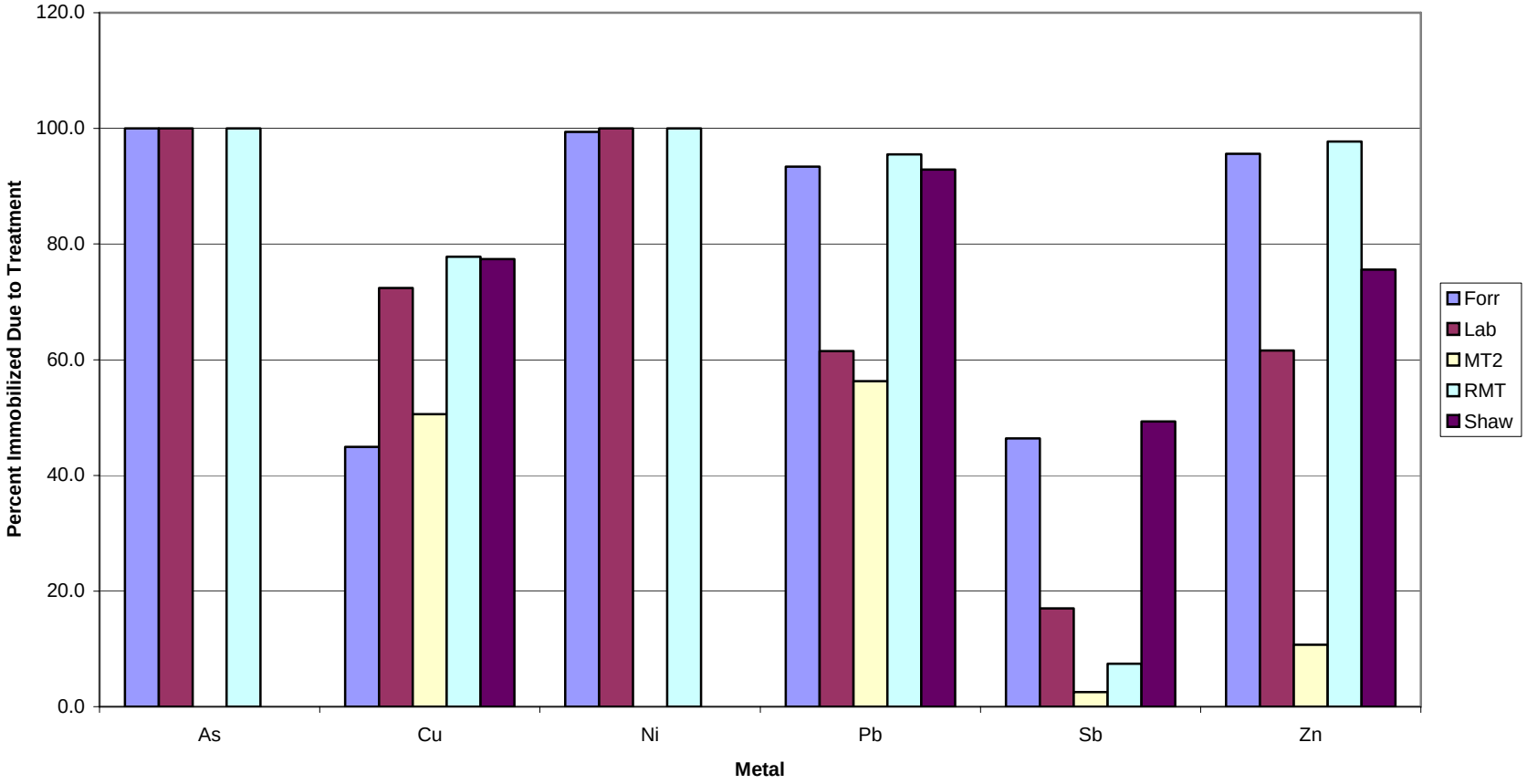


Figure 7-6. Percent immobilized of averaged DI leach COC concentration results.

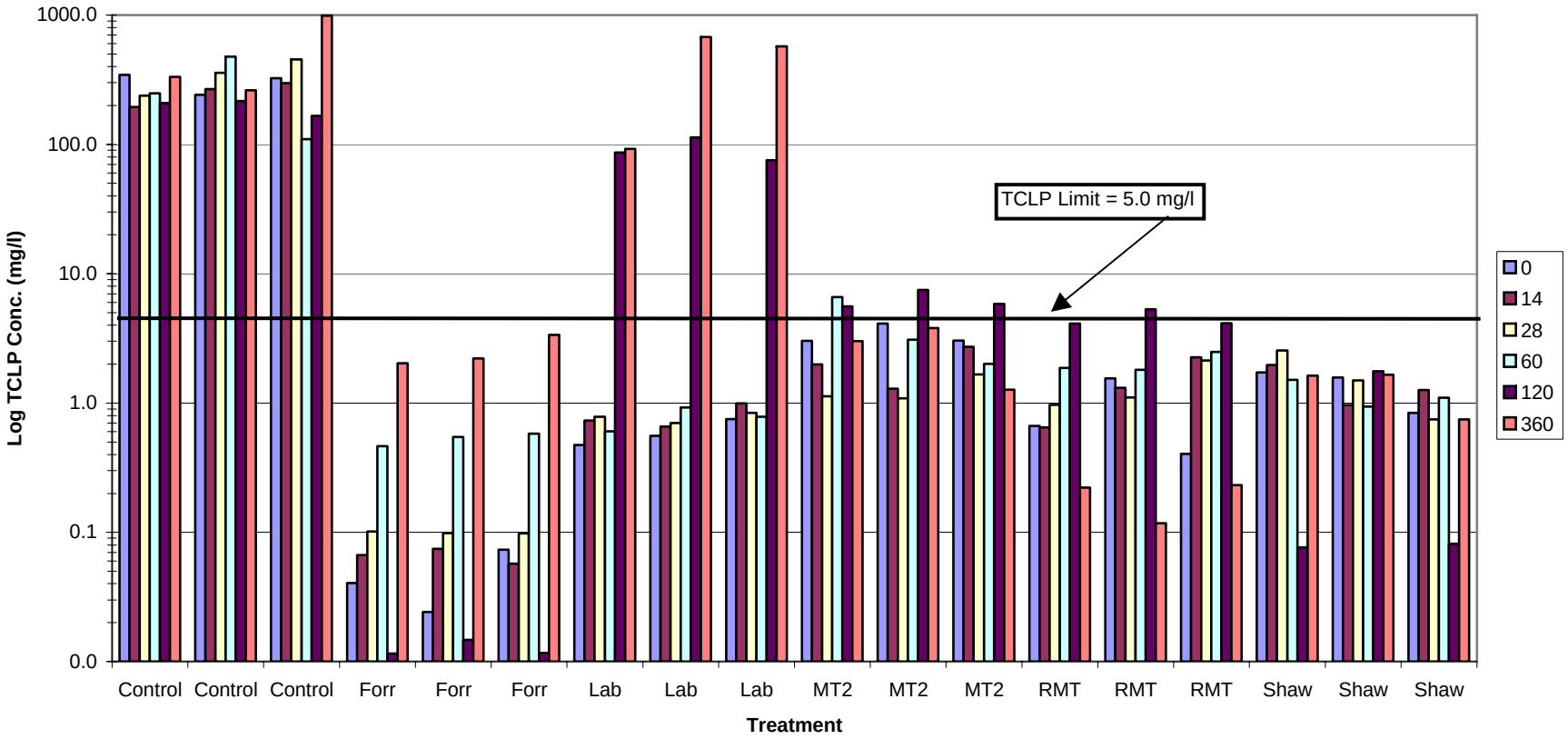


Figure 7-7. TCLP lead concentration results, mg/L.

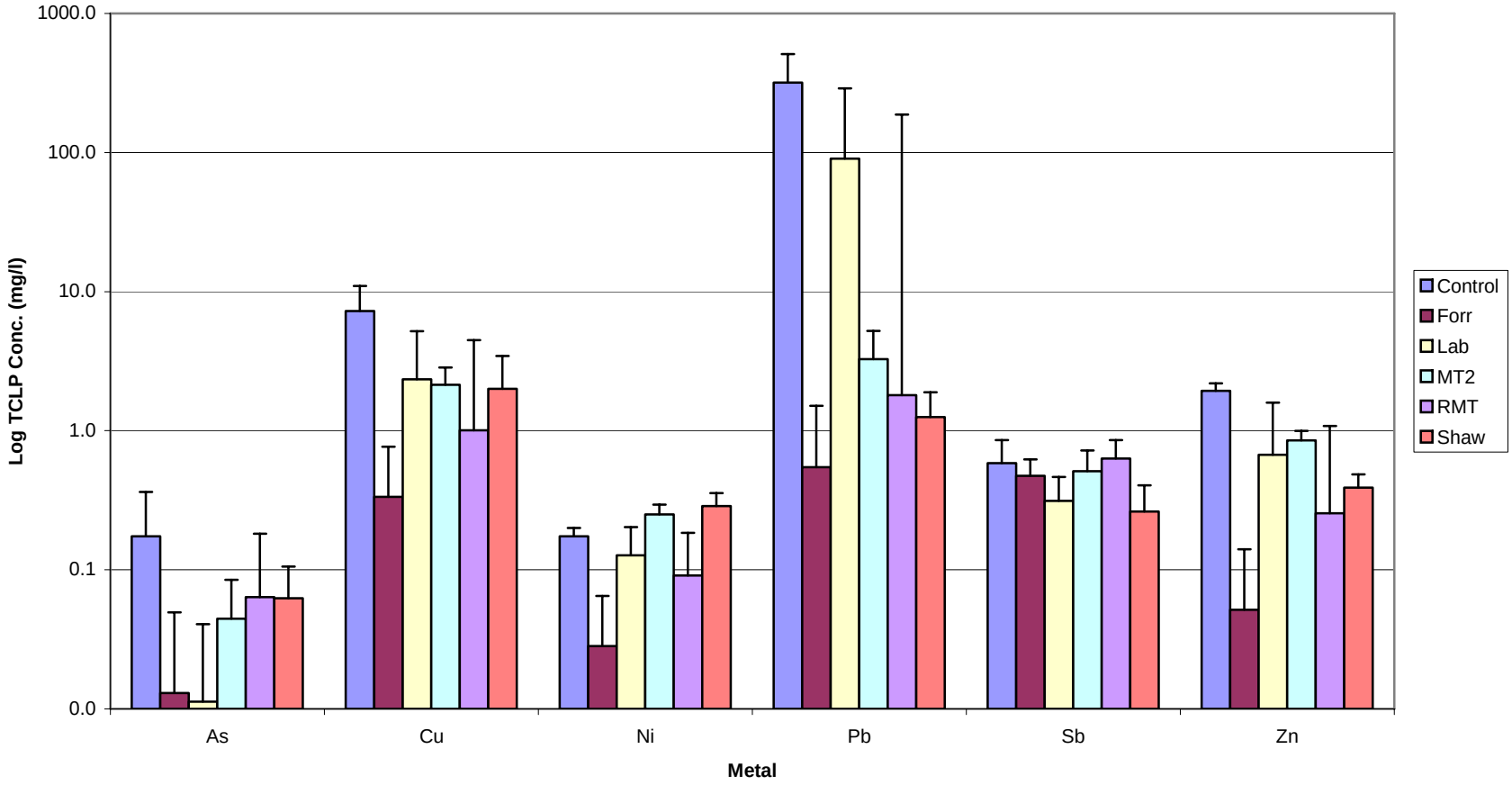
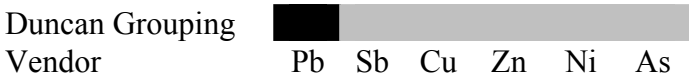


Figure 7-8. TCLP COC concentration results (log scale).

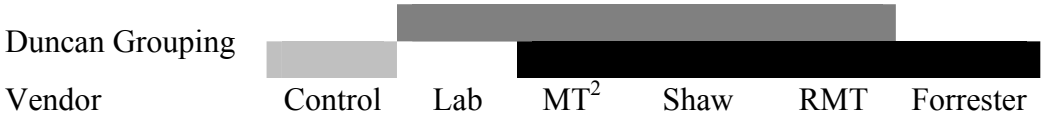
Figure 7-8 illustrates that the Forrester treatment generally provided lower TCLP leachate concentrations for arsenic, copper, nickel, lead, and zinc. Antimony was the only COC that was not reduced by the Forrester treatment. In general, excluding lead and copper, the TCLP COC concentrations were between 0.01 and 1.0 mg/L. Excluding lead, the other treatments (Lab, MT^2, RMT, and Shaw) generally had little to no effect on the COC TCLP concentrations. Graphs showing the TCLP data for each COC are presented in Appendix F.

The results of the Duncan multiple range tests indicated that the data was grouped as follows:

For the COC:



For the vendor treatment of lead:



Where the bars indicate the sample grouping.

The results of the Duncan test indicated that lead is generally leached at higher concentrations than the other COCs. The other COCs were not statistically different in the COC TCLP leachate concentrations. The Duncan test results also indicated that the untreated control samples leached statistically higher concentrations of lead than the treated samples. With regard to the vendor treatments, the Duncan test indicated that the Forrester treatment was significantly different from the Lab treatment. No statistical difference was noted with respect to the other treatments. This is evident in the lead results in Figure 7-8.

Focusing once again on lead TCLP data, an ANOVA was conducted using three classes (treatment = 6 levels, sample age = 6 levels, and replicates= 3 levels). The results of this analysis indicated that the vendor treatment and sample age were statistically different at a 99.9 percent CL. The results of the Duncan multiple range tests indicated that the lead data was grouped as follows:

For the vendor treatment:

For the sample age:

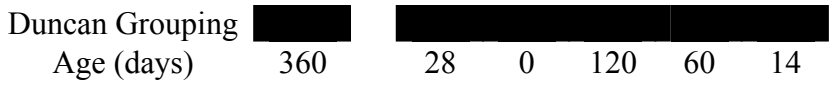


Figure 7-9 illustrates the effectiveness of the Forrester treatment, specifically in the soil samples that had cured $\leq$ 60 days. After this curing period the Forrester-treated sample data

became convoluted. An increase in lead leaching was observed up to the 60-day aged samples then there was a significant drop at day 120. This lead concentration drop was followed by an increase above the 0.75 UTS performance metric (Table 3-1) in the 360-day aged samples. A similar increase in the TCLP lead concentration data for the Lab treatment was observed. The Lab treated soil samples had a two order of magnitude increase in leaching in the 120- and 360-day aged samples. These increases in TCLP lead concentrations were only observed in the Forrester and Lab treatments. No changes in TCLP lead concentration were observed in the control or the MT^2-, RMT-, and Shaw-treated soil over the 360-day monitoring period.

As a result of the significant variations in the Forrester-treated soil data, an additional triplicate set of TCLP analyses were conducted on the control and Forrester-treated soils after 505 days of aging. The averages of the replicate results are presented in Figure 7-10 along with the previously collected data. There was a drop in the 505-day TCLP lead concentration. The Forrester soil treatment results continued to meet the less than the 5.0 mg/L performance metric with TCLP lead concentrations of 2.0 and 1.1 mg/L in the 360- and 505-day aged samples, respectively. However, the Forrester-treated soil lead TCLP concentration was still in excess of the UTS performance metric.

7.1.4 SPLP

The SPLP lead concentration results averaged by replicate are presented in Figure 7-11. Figure 7-11 indicates that the vendor treatments had varying effects on reducing the SPLP lead concentrations. Lead concentrations measured in the SPLP extracts of the control sample ranged from 0.27 to 11.3 mg/L, while many of the treated sample SPLP lead concentrations were at or below the MDL for lead. The Lab- and MT^2-treated samples have consistently elevated SPLP averaged lead concentration results. The Forrester- and Shaw-treated samples were generally consistent in their averaged SPLP lead concentration reductions over the 360-day monitoring period. The RMT-treated samples had generally consistent averaged lead concentration reductions with the exception of a spike in lead concentration in the 60-day aged sample.

A statistical ANOVA for the complete SPLP data set using four classes as presented in Table 7-2 (except COC = 5 levels) indicated that at a 99.9 percent CL the COC and treatments were statistically different (time and replicates were assumed to be the same). As explained in section 7.1.2 the data can be averaged over replicate and sample age. Using this averaging method, the normalized SPLP COC concentration results averaged by replicate and sample age are presented in Figure 7-12 for the control and each vendor-treated soil. The analysis results for many of the samples were below MDL. All analysis results for arsenic and chromium were below MDL. Graphs showing normalized data averaged by replicate for lead, copper, nickel, zinc and antimony are presented in Appendix G.

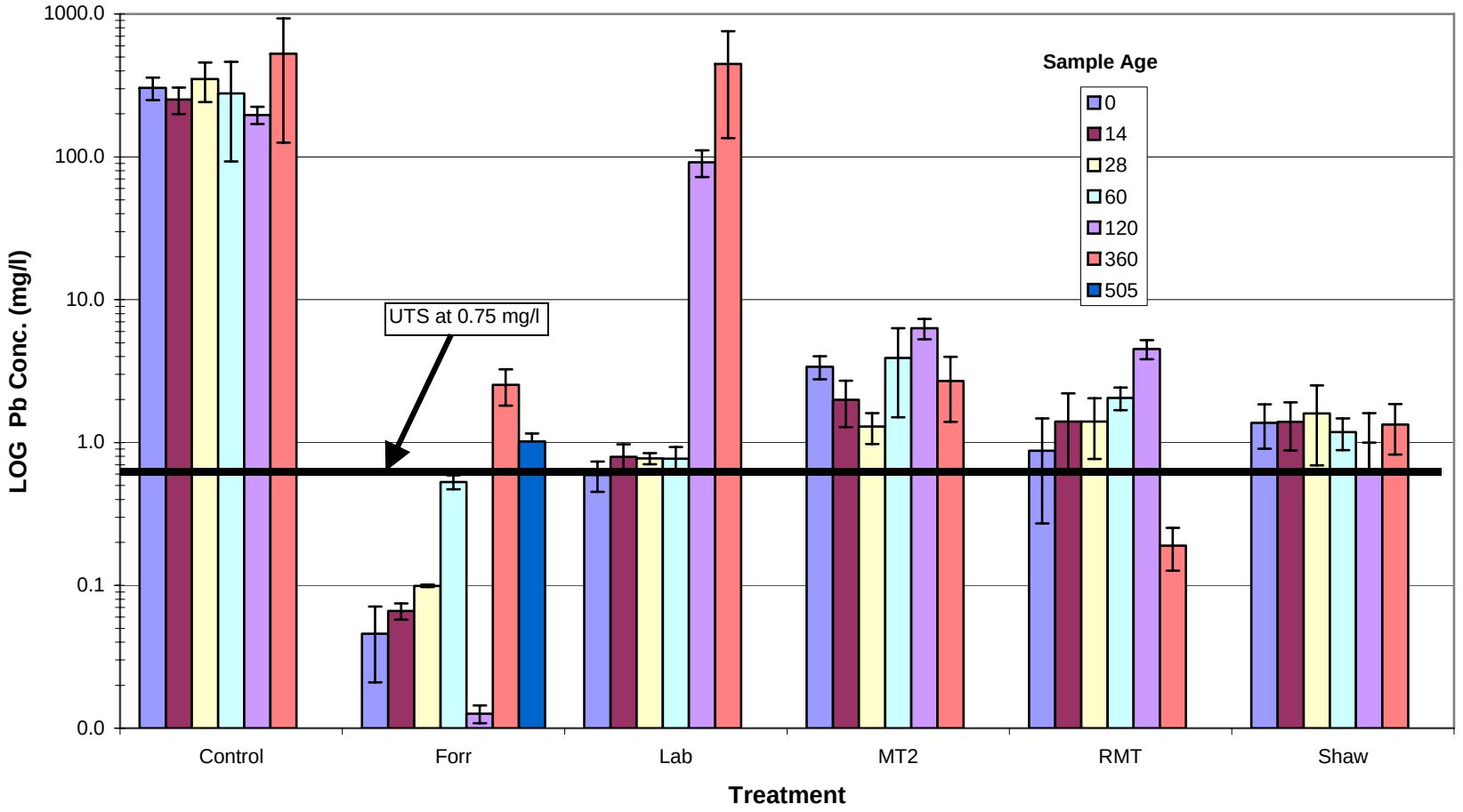


Figure 7-9. TCLP lead concentration results (mg/L, log scale).

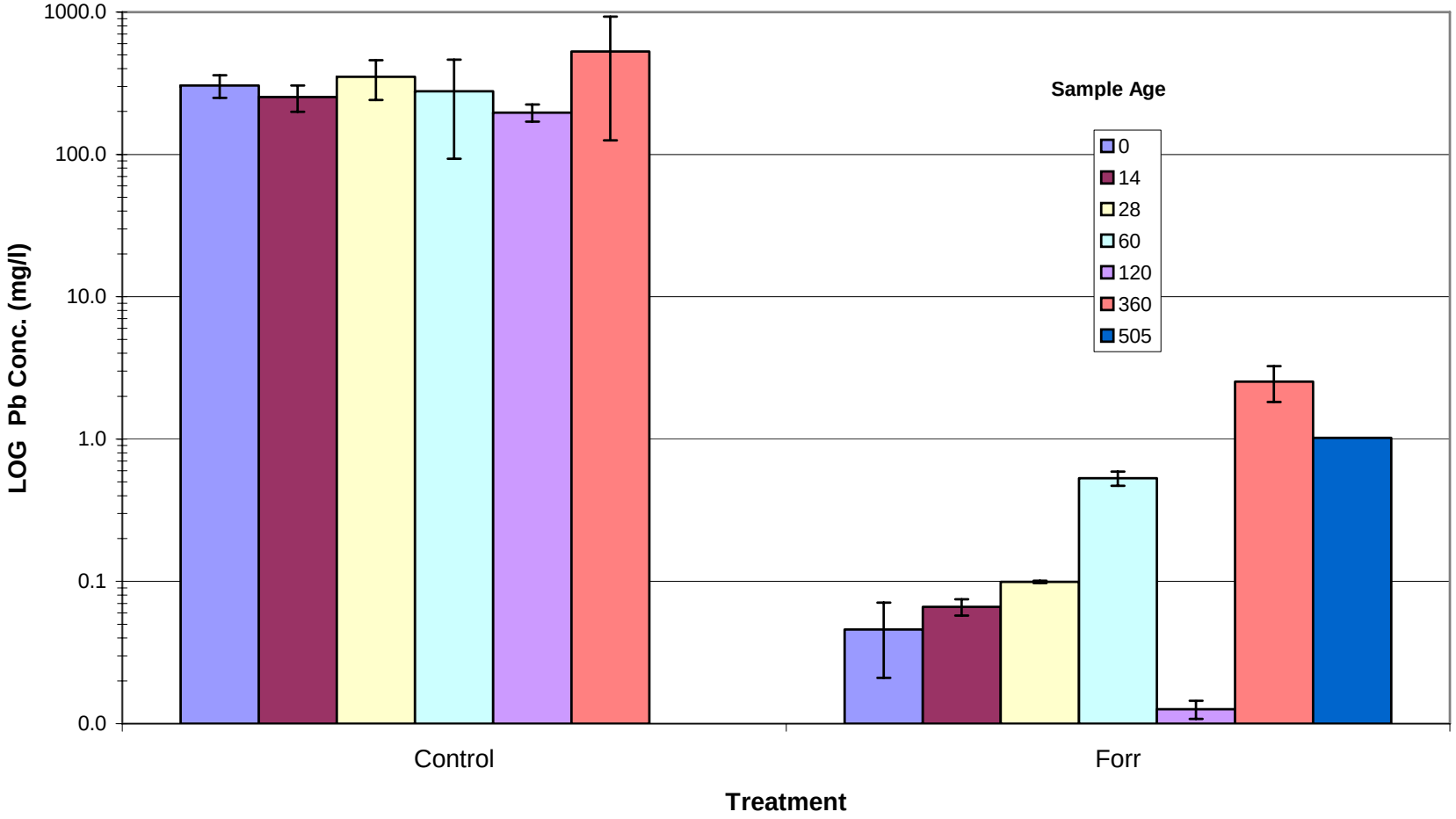


Figure 7-10. Control- and Forrester-Treated soil TCLP lead concentration results (mg/L - log scale).

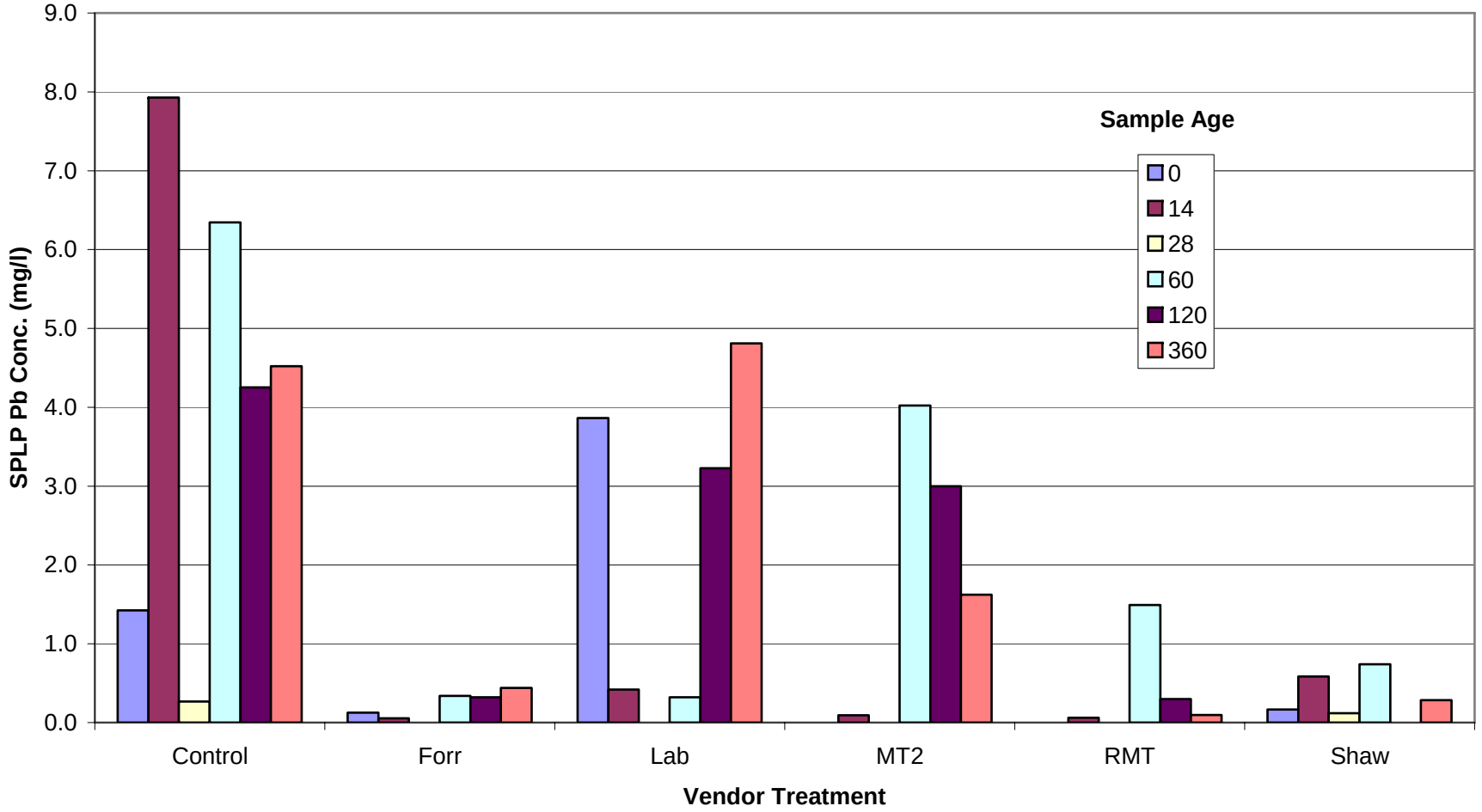


Figure 7-11. SPLP average lead concentration results.

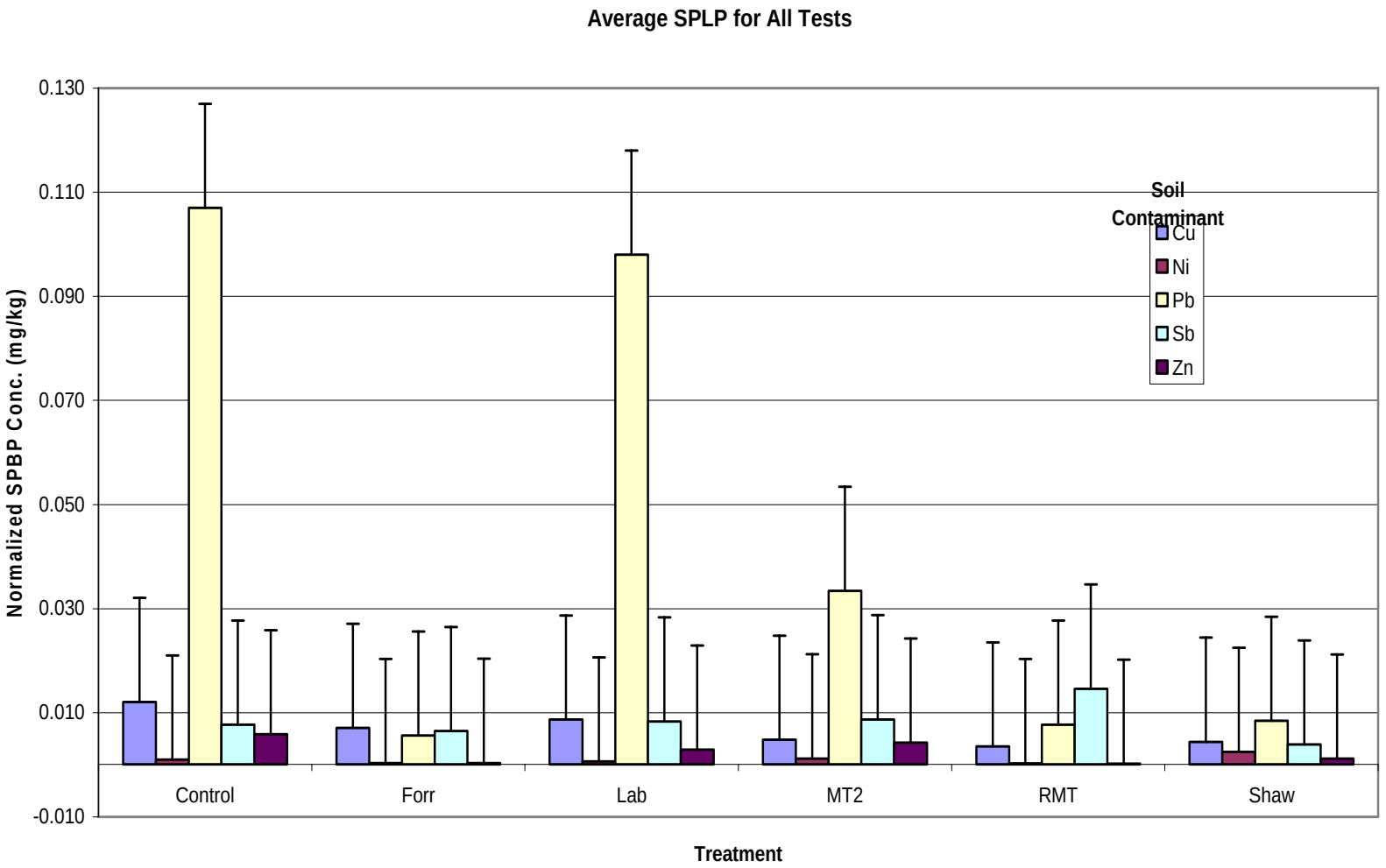


Figure 7-12. Normalized SPLP COC concentration results.

The results of the Duncan multiple range tests indicated that the data was grouped as follows:

For the COC:

For the vendor treatment of lead:

The results of the Duncan tests indicated that lead leached at statistically higher concentrations from the control and treated soils than the other COC. This is also indicated by the normalized SPLP results graphed in Figure 7-12. The Duncan tests also indicated that there was no statistical difference in the SPLP lead concentrations of the control and Lab-treated soils. However, the SPLP lead concentrations from the vendor-treated soils were statistically lower than that found in the control soil. No statistical difference was evident with respect to the different vendor treatments.

7.1.5 SET

As discussed in Materials and Methods, the SET consisted of a series of five extractions where the aggressiveness of each extraction in the series was increased. A single sample of soil was carried through all five extractions; thus, the final extraction should have resulted in the extraction of all the lead contained in the soil. If the vendor treatments were successful, then the lead was transformed to relatively insoluble species such as a lead pyromorphite. In this case the SET lead concentration results would indicate this decrease in lead solubility by shifting the concentration of extractable lead from SET fractions No. 1, 2, and 3 to SET fractions No. 4 and 5.

Figure 7-13 presents a graph for the Forrester-treated soil SET lead concentration results averaged by replicate. The averaged data in Figure 7-13 is presented for each extract at each sample cure time interval. In this form, it is difficult to interpret treatment effectiveness other than to note a general shift in lead solubility to the more aggressive extractions when compared to the control SET results. In order to facilitate data comparison and interpretation, the data was normalized to the mass of lead extracted (in mg) divided by the weight of dry raw soil (in g). This normalized SET lead concentration data for the Forrester-treated soil is presented in Figure 7-14. Figure 7-15 presents the control soil normalized SET lead concentration data to allow a direct comparison with the treated soil data (Figure 7-14). The direct comparison of data indicates that the treatment of the soil by Forrester resulted in the extractable lead being shifted from the fractions No. 1 and 2 in the control to fractions No. 3, 4, and 5 in the Forrester-treated soil.

A statistical ANOVA was conducted on the entire data set using four classes (the extraction step = 5 levels, the vendor = 6 levels, the cure time = 6 levels, and the

replicates = 3 levels). The results of this analysis indicated that, at the 99.9 percent CL, only the extraction steps were significantly different. The ANOVA produced data that were somewhat difficult to interpret. In order to support data interpretation, the data were separated into five different data sets by extraction fraction. The ANOVA was conducted on these separate data sets now using 3 classes (the vendor = 6 levels, the cure time = 6 levels, and the replicates = 3 levels). The results of this analysis indicated that, at the 99.9 percent CL, only the vendor treatments were significantly different for extraction fractions No. 1, 3, and 5 as shown in Table 7-3. This indicates that for these data sets the SET results could be averaged by replicates and cure times.

TABLE 7-3. STATISTICAL ANOVA RESULTS FOR THE SET

Step	Vendor	Time	Replicate
1	X	---	---
2	---	---	---
3	X	---	---
4	---	---	---
5	X	---	---

Note: X means data are statistically different at the 99.9 percent CL.

The control and vendor-treated soil SET lead concentration results for each extraction fraction was averaged by replicate and cure time and then normalized to yield the lead concentration (mg/g) from the soil. These data were then used to calculate the percentage of lead concentration removed from the control and vendor-treated soil samples with respect to each SET extraction fraction. The distributions are graphed in Figure 7-16. Again, the data trends indicate a shift in lead concentrations from the more soluble fractions in the control (fractions No. 1 through 3) to the less soluble fractions in the treated soils (fractions No. 4 and 5). These data are summarized by grouping the more soluble and less soluble fraction data in Figure 7-17. Figure 7-17 shows that over 65 percent of the lead in the control soil was extracted from the more soluble fractions. However, a shift in solubility is observed in the treated soils. In these soils the extractable lead concentrations have dropped to approximately 25 percent, with the exception of the RMT-treated soils whose extractable lead concentrations dropped to approximately 43 percent. These data indicate that the phosphate treatments have resulted in a substantial reduction in the solubility characteristics of the lead in the soil, from which it can be inferred that less soluble lead species have formed as a result of the treatments.

7.1.6 PBET

7.1.6.1 Analysis Results

The evaluation of health risk reduction was made based on the measured reduction of bioaccessible lead. The bioaccessible fraction of the lead in the control and treated soils was measured using the PBET. The PBET is a laboratory extraction test designed to simulate the digestive tract of humans. The bioaccessability reduction was evaluated through comparison between the control and treated soil PBET results. As explained in Materials and Methods, the

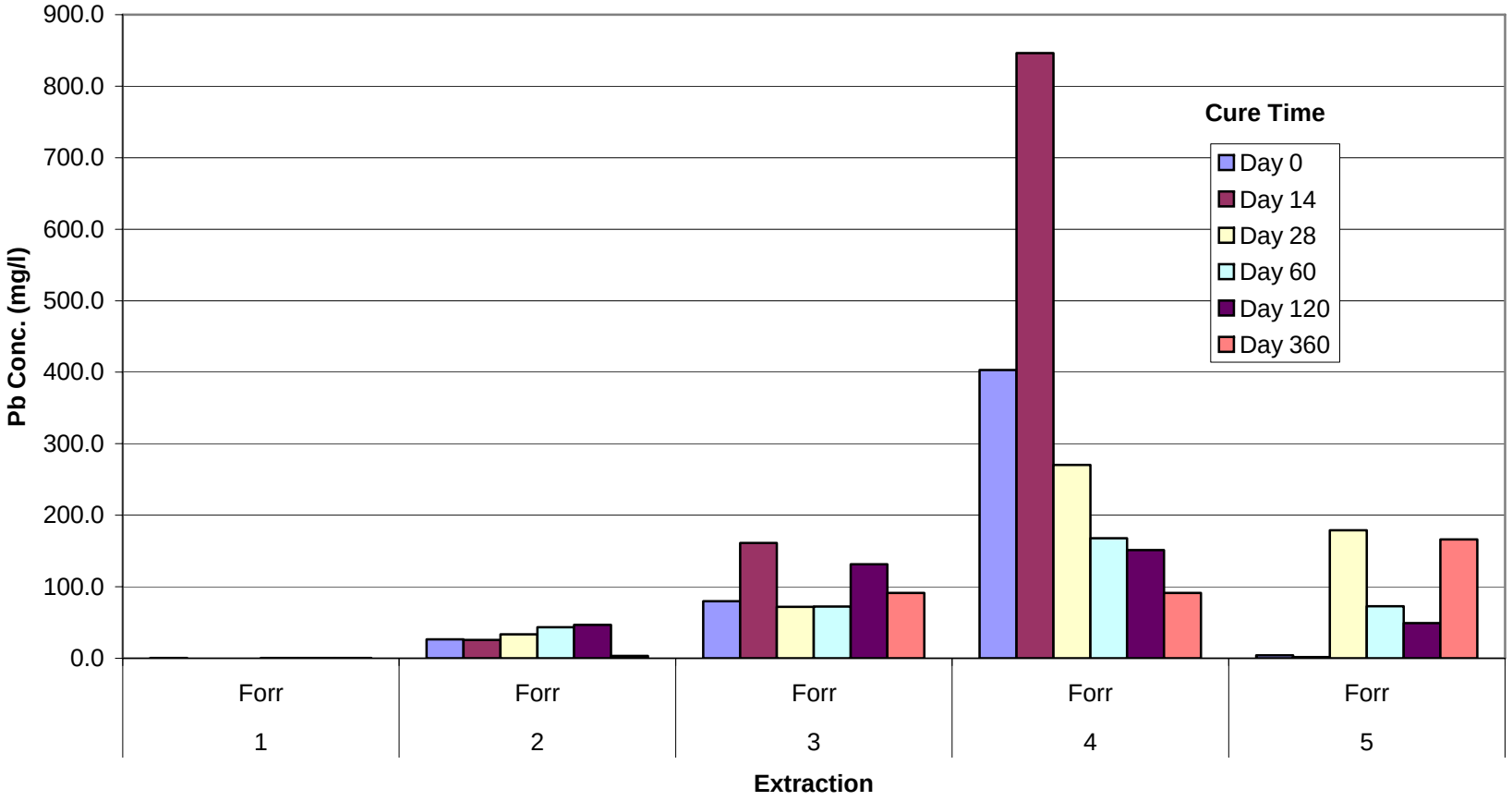


Figure 7-13. SET lead concentration results for Forrester-treated soil.

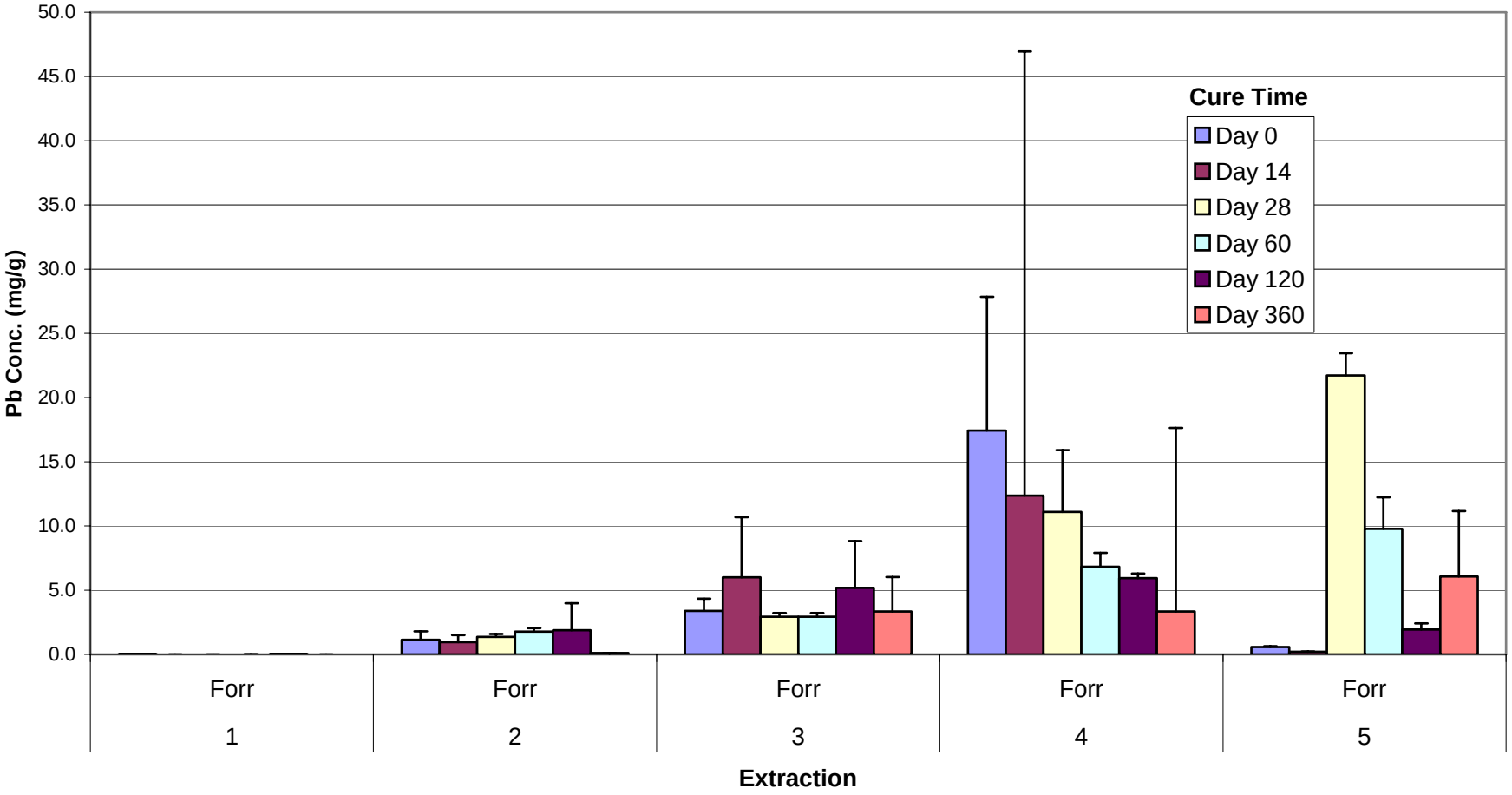


Figure 7-14. Normalized SET lead concentration results for Forrester-treated soil.

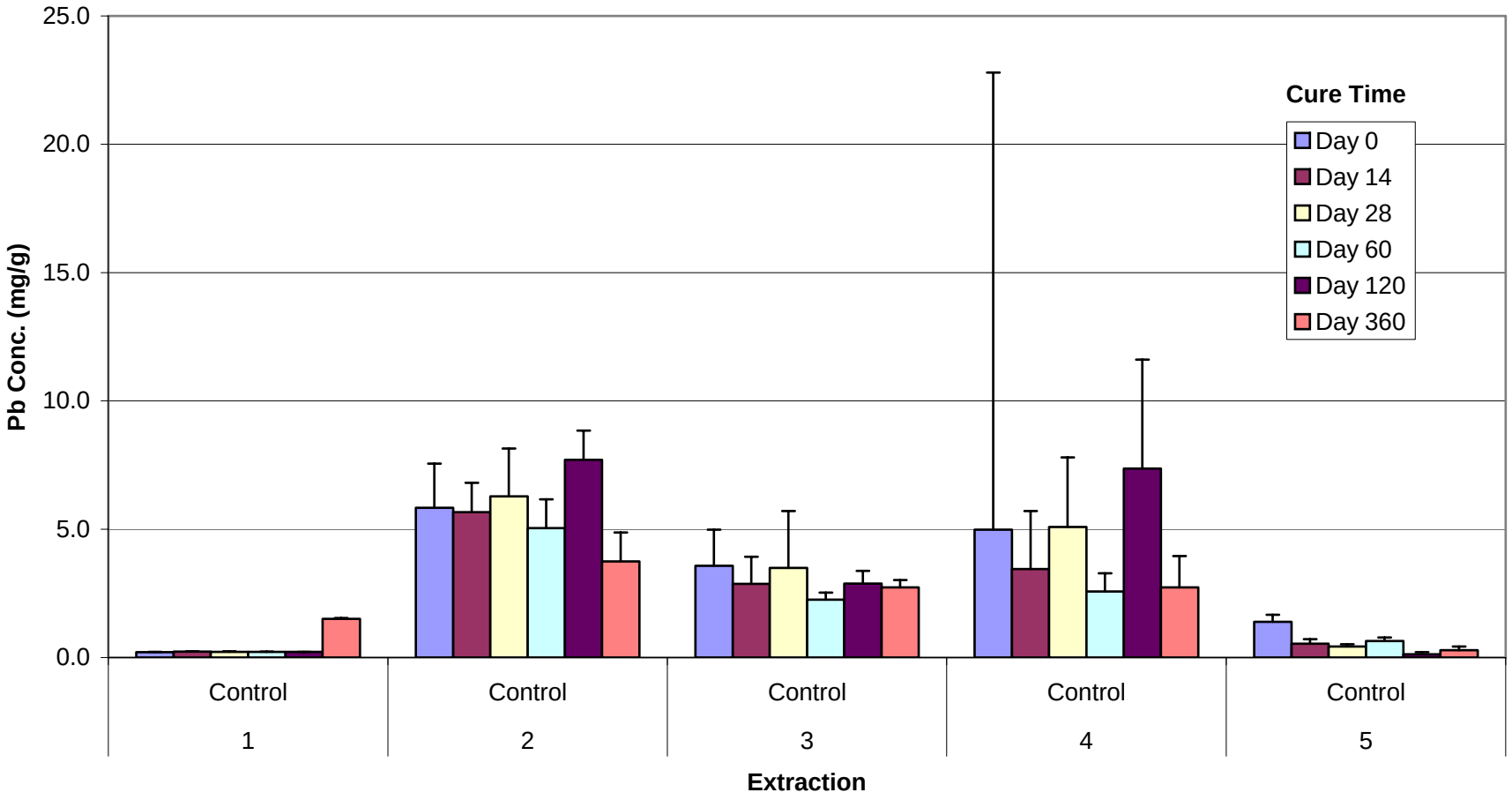


Figure 7-15. Normalized SET lead concentration results for the control soil.

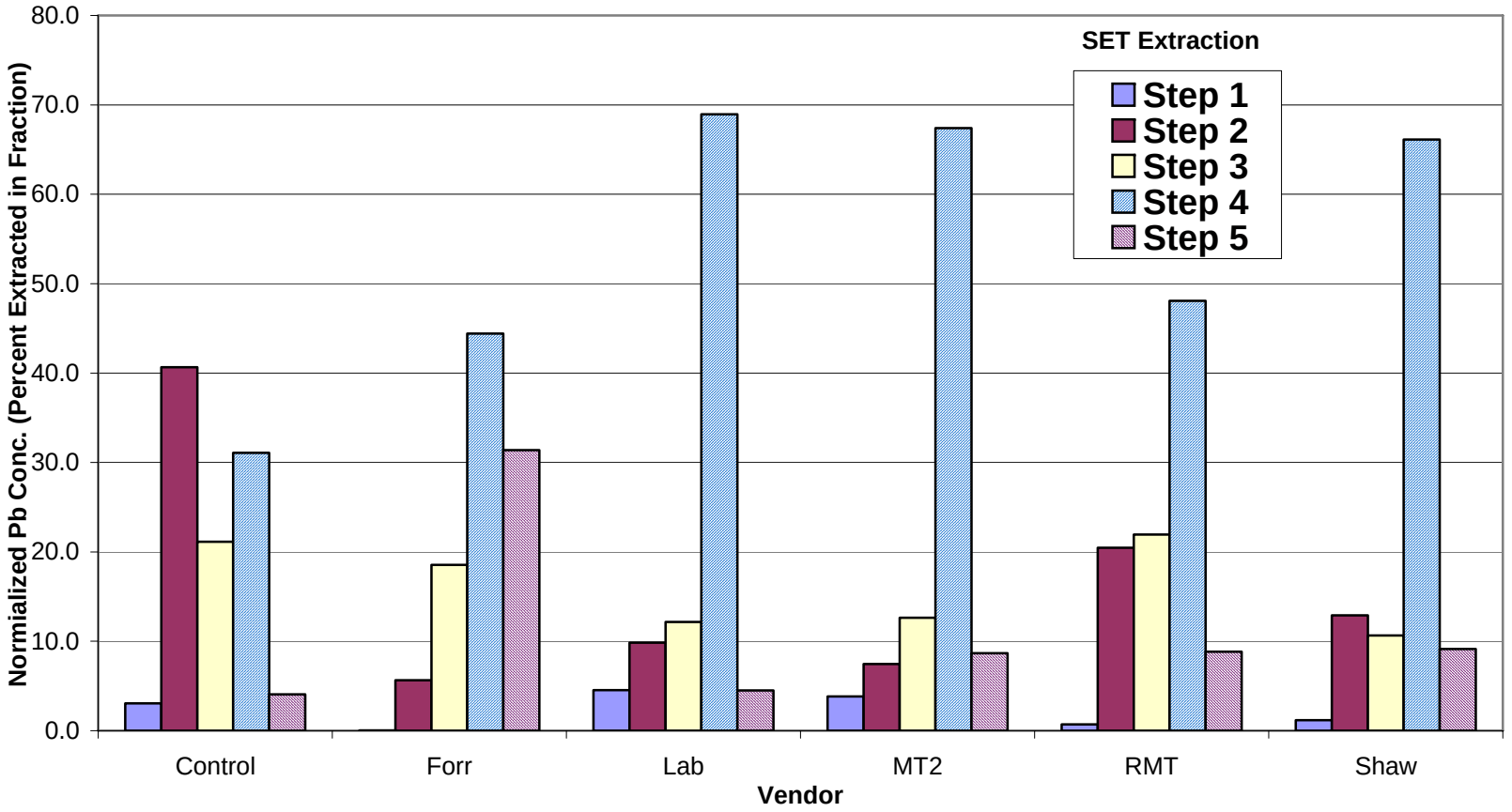


Figure 7-16. Normalized SET lead concentration distribution in the SET fractions for the control and vendor-treated soils.

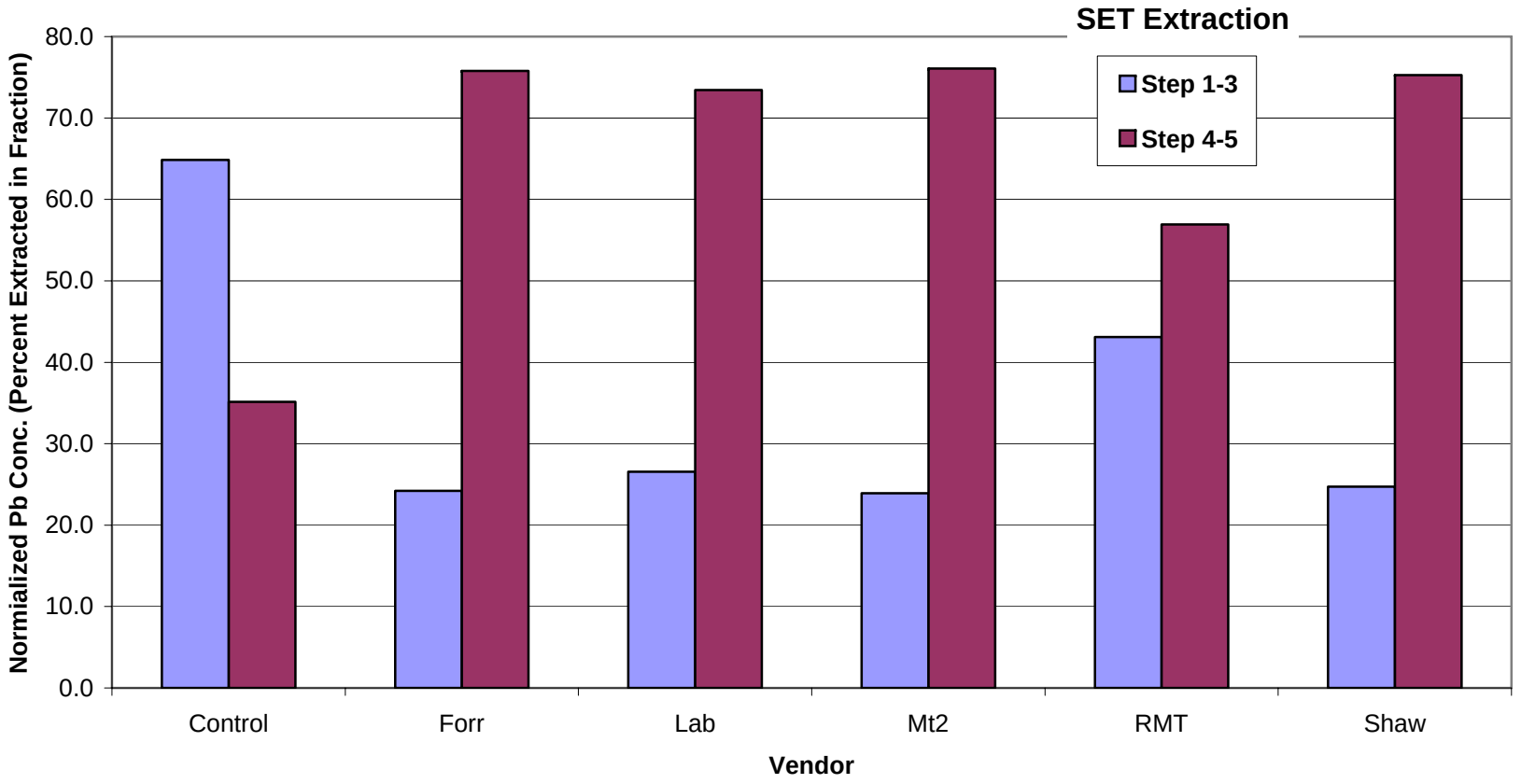


Figure 7-17. Normalized SET lead concentration distribution in grouped SET fractions for the control and vendor-treated soils.

PBET was conducted at both the 1.5 pH and 2.3 pH levels. Extractions at both pHs were performed based on the interim results of ongoing correlations studies designed to validate the PBET procedure.

The USEPA has not validated the PBET in vitro test as an acceptable substitute for in vivo lead bioaccessibility methods. The correlation between PBET results and in vivo results have not been found to hold up over a wide range of soil parameters. Phosphate amended soils has been shown to be somewhat inconsistent in comparison of in vitro and in vivo results. However, the PBET method has provided fairly close correlations and was used in this analysis as a low cost screening tool. Prior to moving forward with considering phosphate based amendments in a field demonstration or as a cleanup method, the bioaccessibility needs to be re-evaluated using accepted in vivo methods.

Figures 7-18 and 7-19 present the PBET lead concentration data averaged by replicate using the 1.5 pH and 2.3 pH extraction methods, respectively. The control sample data in theory should have provided equal PBET lead concentrations as the sample age because no amendment was added. However, at both extraction pHs, the PBET lead concentrations varied with age. This data variability was particularly apparent for the control sample 2.3 pH PBET lead concentration results. There were no discernable patterns observed in the control sample results (with sample aging). These variations in PBET lead concentrations were most likely caused by heterogeneities in the samples.

At both extraction pHs, the 120- and 360-day sample PBET results tend to increase in lead concentration. This trend was more pronounced in the 2.3 pH extraction, although the lead concentrations were higher in the 1.5 pH extractions.

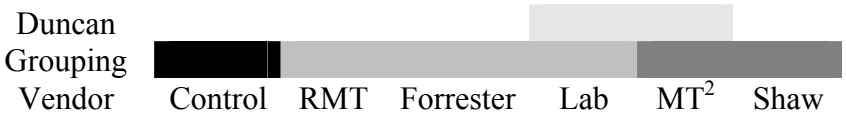
The PBET lead concentrations in the treated samples extracted at 1.5 pH (Figure 7-18) indicated that only a small reduction in bioaccessible lead occurred when compared to the control data. The only noticeable exception is the 0-, 14-, and 28-day results for the Lab-treated soil where a significant reduction in lead leachate concentration was apparent. All treated soils exhibited significant variations in PBET lead concentration results over the monitoring period. The cause of these variations may be heterogeneities in the samples similar to that observed in the control sample. More likely these changes in lead leachate concentrations resulted from changes in lead species stability over time since there appeared to be a general pattern of decreasing lead concentration during the first 28 days followed by an increase in lead concentration through the remainder of the monitoring period.

The PBET lead concentrations in the treated samples extracted at 2.3 pH (Figure 7-19) indicated that a slightly larger reduction in bioaccessible lead occurred when compared to the control data. Shaw, MT^2, and Forrester generally produced the greatest reductions in PBET lead concentrations. All treated soils exhibited significant variations in PBET lead concentration results over the monitoring period. Again, the cause of these variations may be heterogeneities in the samples similar to that observed in the control sample. However, since a similar general pattern of decreasing lead concentration followed by an increase in lead concentration through the remainder of the monitoring period occurred as noted in the 1.5 pH extractions, these changes in lead leachate concentrations were again more likely the result of changes in lead species stability over time.

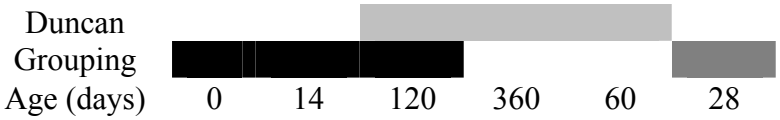
To directly compare the PBET results, the PBET data were normalized to the dry raw soil lead concentration as described in section 7.1.2 of this report. A statistical ANOVA on the complete normalized data set was performed. There were four classes used in the analysis (pH = 2 levels, vendor treatment = 6 levels, sample age = 6 levels, and replicates = 3 levels). The ANOVA indicated that pH, vendor treatments, and sample age were significantly different at the 99.9 percent CL, but the replicates were not.

The results of the Duncan multiple range tests indicated that the data was grouped as follows:

For the vendor treatment:



For the sample age:



The results of the Duncan test indicated that the MT2 and Shaw treatments were in a separate group from the RMT, Forrester, and Lab treatments. All of the treated samples were significantly different than the control samples. In general, all of the treated samples had less PBET lead concentrations than the control samples and ranked as follows:

Vendor	Shaw	MT^2	Lab	Forrester	RMT		Control
Lead (mg/L)	4.9	5.5	6.2	6.6	7.0	>	9.1

Based on the data presented in Figures 7-18 and 7-19 it was expected that the ANOVA and Duncan test would have identified a clear difference in the 120- and 360-day aged samples when compared to the 0-, 14-, 28- and 60- day samples. Unfortunately, the data was confounding and no conclusive differences were identified.

The data were also presented using the normalized PBET results as the percent of lead immobilized when compared to the control samples. These data are presented in Figure 7-20 and 7-21 for the 1.5 and 2.3 pH test, respectively. The 1.5 pH data showed that the Shaw treatment was the only vendor with a reduction in PBET lead concentration over the entire 360-day monitoring period. All of the vendor treatments indicated increases in 1.5 pH PBET lead concentrations from low points at the 14-day cure time. The 2.3 pH data show that the MT^2 and Shaw treatments were the only vendors with a reduction of PBET lead concentration over the entire 360-day monitoring period. All of the vendor treatments, with the exception of the Shaw treatment, indicated increases in 2.3 pH PBET lead concentrations from varying low-points during the 360-day monitoring period.

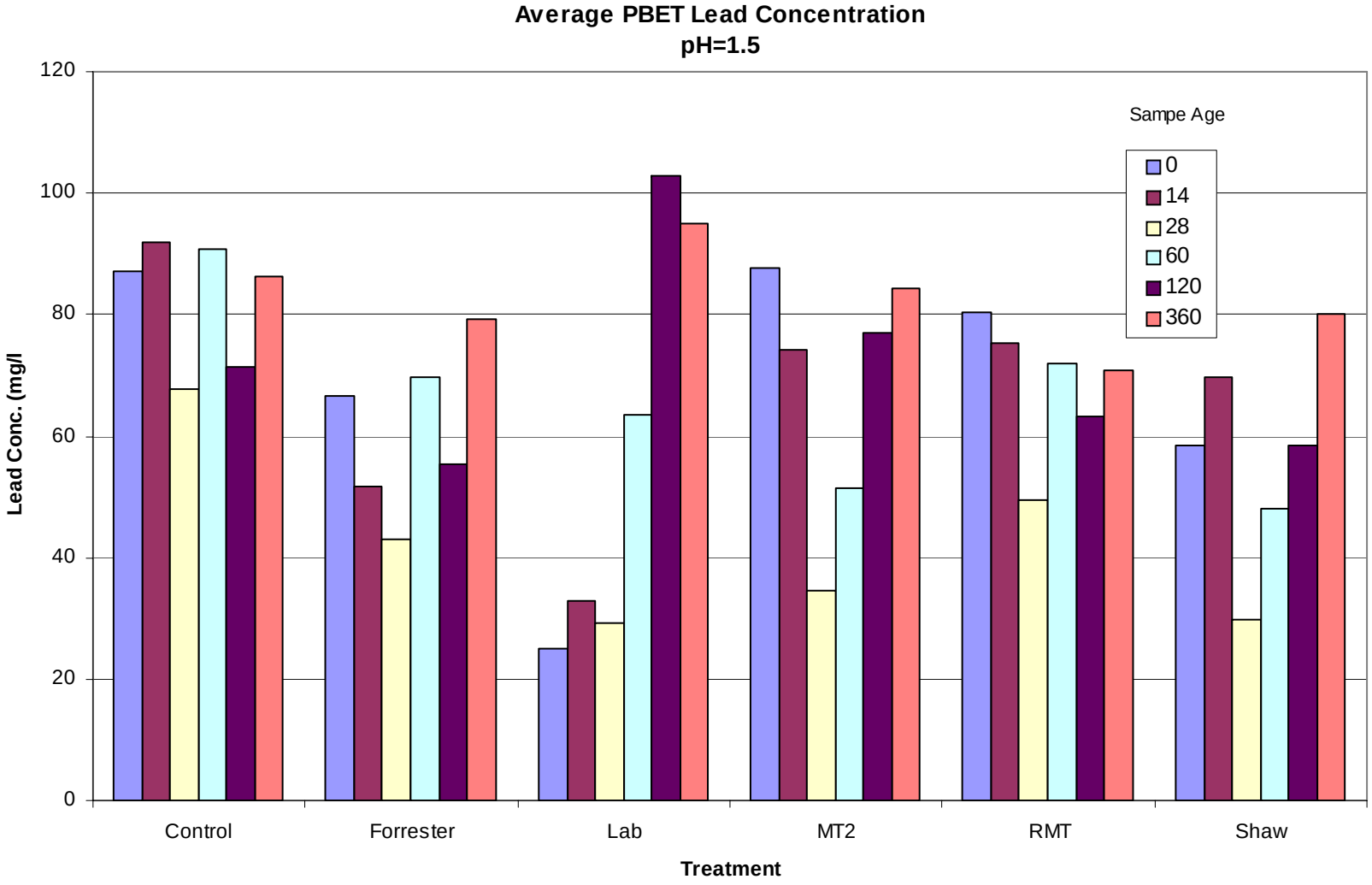


Figure 7-18. PBET lead concentration results (1.5 pH).

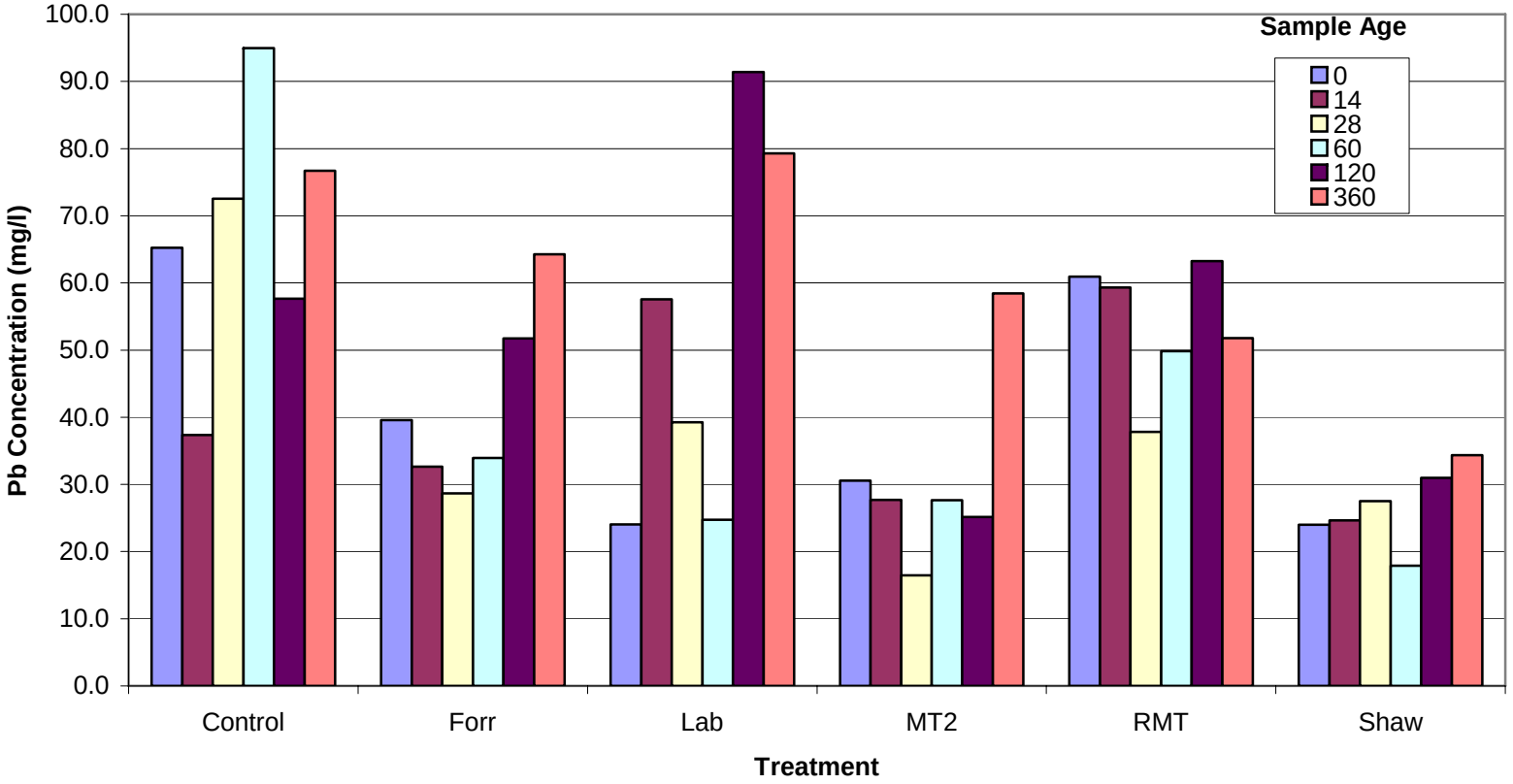


Figure 7-19. PBET lead concentration results (2.3 pH).

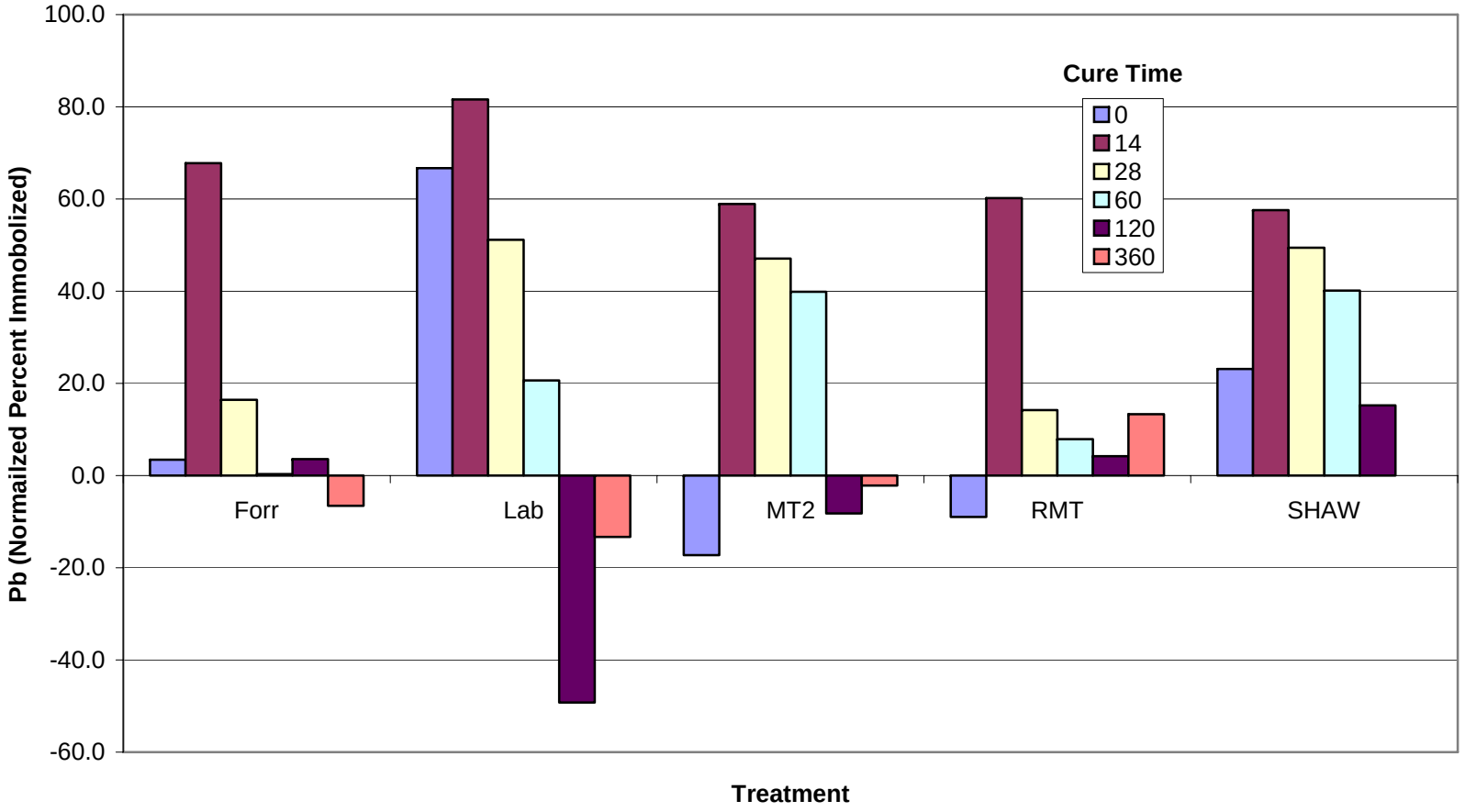


Figure 7-20. Normalized (1.5 pH) PBET lead concentration results (percent of lead immobilized).

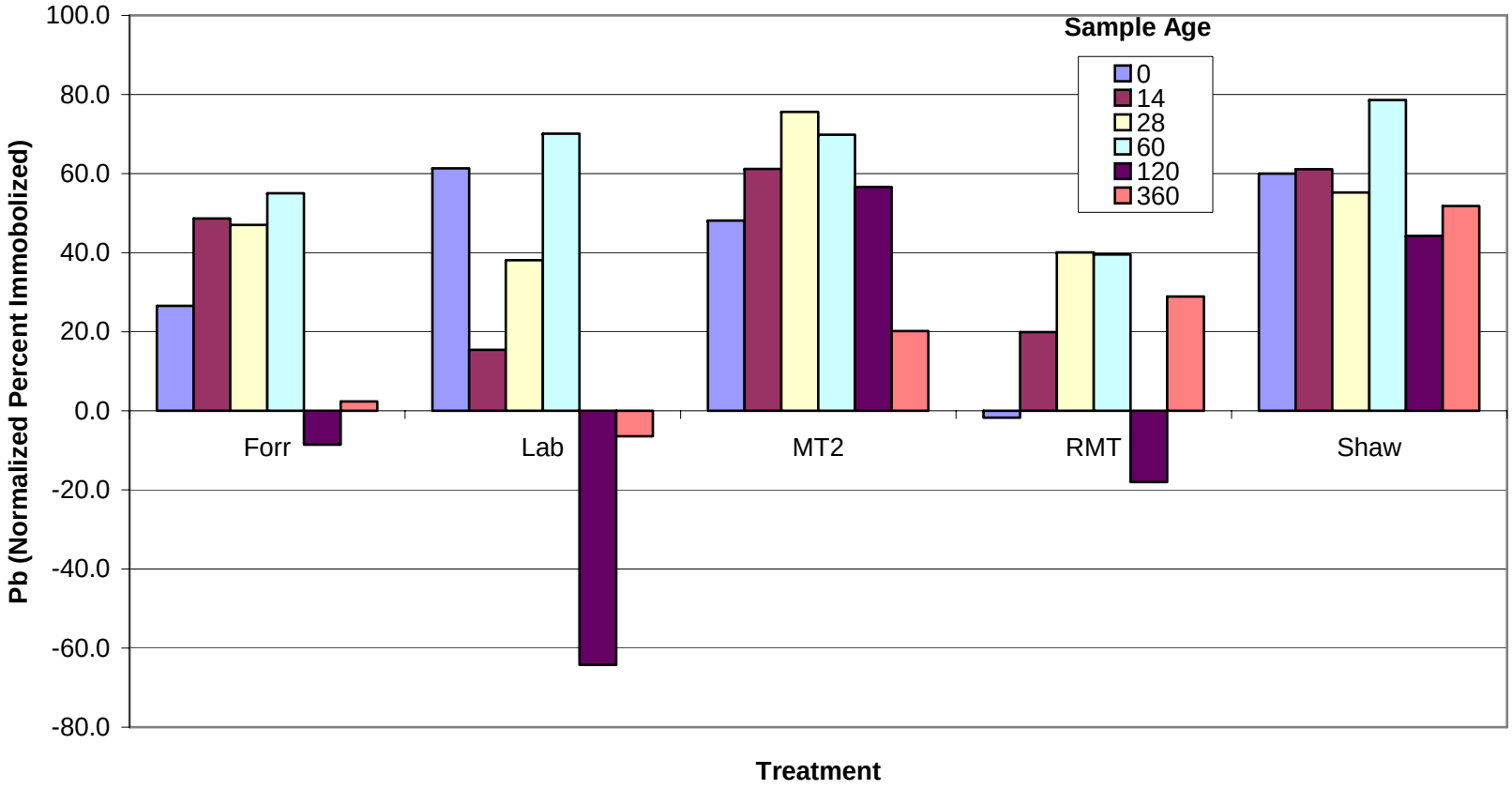


Figure 7-21. Normalized (2.3 pH) PBET lead concentration results (percent of lead immobilized).

7.1.6.1 IEUBK Model Results

The PBET lead concentration data were used to estimate the risk associated with the stabilized lead contained by the soil. The reduction in bioaccessibility as measured by the PBET was input into the IEUBK model to estimate the risk associated with treated soil. The Center for Disease Control (CDC) defines an acceptable blood lead level (PbB) in children to be 10 µg/dL. No more than 5 percent of the population should exceed this PbB (CDC 1991).

As noted in the previous section, the PBET is not an USEPA accepted method for determining lead bioaccessibility. This method was used in this program as a low cost screening tool to facilitate the technology assessment. As a result, the model results presented here do not serve as an actual risk assessment recognized by the USEPA. Prior to selecting phosphate amendments as a cleanup option, the risk assessment must be performed using accepted in vivo results. The modeling of risk presented here is only for comparison purposes and an indication of relative risk at the range site being investigated.

Using the average soil lead concentration of 11,700 mg/kg and running the model with the PBET bioaccessible lead data for each vendor-treated sample, the model predicts that 93.9 percent to 99.5 percent of the population will have PbB greater than the 10 µg/dL. In general, the resulting reductions in PBET lead concentrations as a result of the vendor treatments had very little effect in decreasing the absolute bioaccessibility of the lead. Population risk as determined by the model was influenced by the soil lead concentration to a much greater extent than the bioaccessible lead data. (Note: In conversation with Dr. Mark Follansbee of the USEPA Technical Review Working Group for Lead, Dr. Follansbee indicted that a relative bioavailability should be used or the IEUBK model may overestimate the lead impacts. This involved conducting a PBET analysis on a lead acetate spiked soil sample. Unfortunately, this was not clear in the IEUBK guidance documents and was not prepared as part of this study.)

At the soil lead concentrations present in the Camp Withycombe soil, the reduction in bioaccessible lead would need to be significantly greater than that observed in the treated soils to meet the USEPA PbB level criteria. The IEUBK model was used to determine a target bioaccessibility value using the 11,700 mg/kg average soil lead concentration that would result in less than 5 percent of the population having PbB at 10 µg/dL. The model results yielded the need to reduce bioaccessible lead to between 0.5 percent and 1.0 percent of the average soil lead concentration. In this study the absolute bioavailability resulting from the vendor treatments as measured by the PBET was reduced from 100 percent to between 93.9 percent and 99.5 percent. This reduced the model's default bioaccessibility from 30 percent to between 27.9 percent and 29.7 percent. This was much less than the 0.5 percent required. In order to meet the USEPA PbB criteria, the Camp Withycombe soil PBET lead concentrations must be no greater than 1.9 mg/L. The average PBET lead concentration for all of the vendor treatment results was 41 mg/L.

7.1.7 Phosphate

In addition to the extraction tests conducted for the metal contaminants, the control and treated samples were subjected to a series of phosphate tests. The control and vendor treated samples were subjected to a total digestion (Method 3051) and subjected to phosphate analysis to determine the total phosphors in the samples. In addition, control and vendor-treated samples were subjected to a DI water extraction (DI Extract). The liquid extract from the DI Extract was analyzed for leachable (or free) phosphate. Then the DI extract was subjected to a liquid digestion (Method 3050) and analyzed to determine the hydrolysable phosphate. The average phosphate results for the total phosphors, leachate phosphors, and hydrolysable phosphors are presented in Figures 7-22, 7-23 and 7-24, respectively.

7.1.7.1 Total Phosphate

The results for the total phosphate analysis (Figure 7-22) indicated that all samples, except for the control, contained substantial quantities of phosphate. The total phosphate concentrations in Figure 7-22 are presented on a log scale versus the control and vendor treatment soils. The phosphate concentrations in vendor treated soils ranged from a high 48,000 to a low of 9,800 mg/kg. The control contained an average of 14 mg/kg phosphate concentration.

An ANOVA using three classes (vendor treatment = 6 levels, sample age = 6 levels, and replicates = 3 levels) indicated that both vendor and time treatments were significantly different at the 99.9 percent CL. For vendor treatment a Duncan multiple range test indicated that each vendor was in a separate group as shown:

Duncan Grouping	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
Vendor	Shaw	Forrester	MT^2	RMT	Lab	Control

This data can be used to indicate the quantity of phosphate binder added by each vendor. The ranking of phosphate addition (in mg/kg) for each vendor are:

Shaw	>>	Forrester	>	MT^2	>	RMT	>	Lab	>>	Control
(47,100)		(31,400)		(24,500)		(13,400)		(10,200)		(14)

7.1.7.2 Leachable Phosphate

Leachable phosphate concentrations are summarized in Figure 7-23. In this figure the free phosphate concentrations leached in the DI Extract tests are presented on a log scale versus the control and vendor treatment soils. All vendor-treated soils leached substantial quantities of phosphate except for the Forrester-treated soils. In fact, the 120- and 360-day Forrester samples had lower free phosphate concentrations than those leached from the control samples. In addition, Figure 7-23 clearly indicates that substantial concentrations of phosphate were mobile in the Shaw-, MT^2-, and Lab-treated soils.

An ANOVA was conducted on the data using three classes (vendor treatment = 6 levels, sample age = 6 levels, and replicates = 3 levels). This analysis indicated that only the vendors

show statistically significant differences at the 99.9 percent CL. The results of the Duncan multiple range tests indicated the following grouping:

Duncan Grouping	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
Vendor	Shaw	MT^2	Lab	RMT	Forrester	Control

This reinforced the graphical observation that the ranking for the phosphate vendors are:

Forrester	=	Control	<	RMT	<	Lab	<<	MT^2	<<	Shaw	
1.6		1.8		65		380		4,800		18,400	leachable phosphate (mg/kg)

7.1.7.3 Hydrolysable Phosphates

The hydrolysable phosphate concentrations are similar to the leachable phosphate as shown in Figure 7-24. Even though hydrolysable phosphate is mobile and can be transported, it is not available to biota. These data are included for completeness.

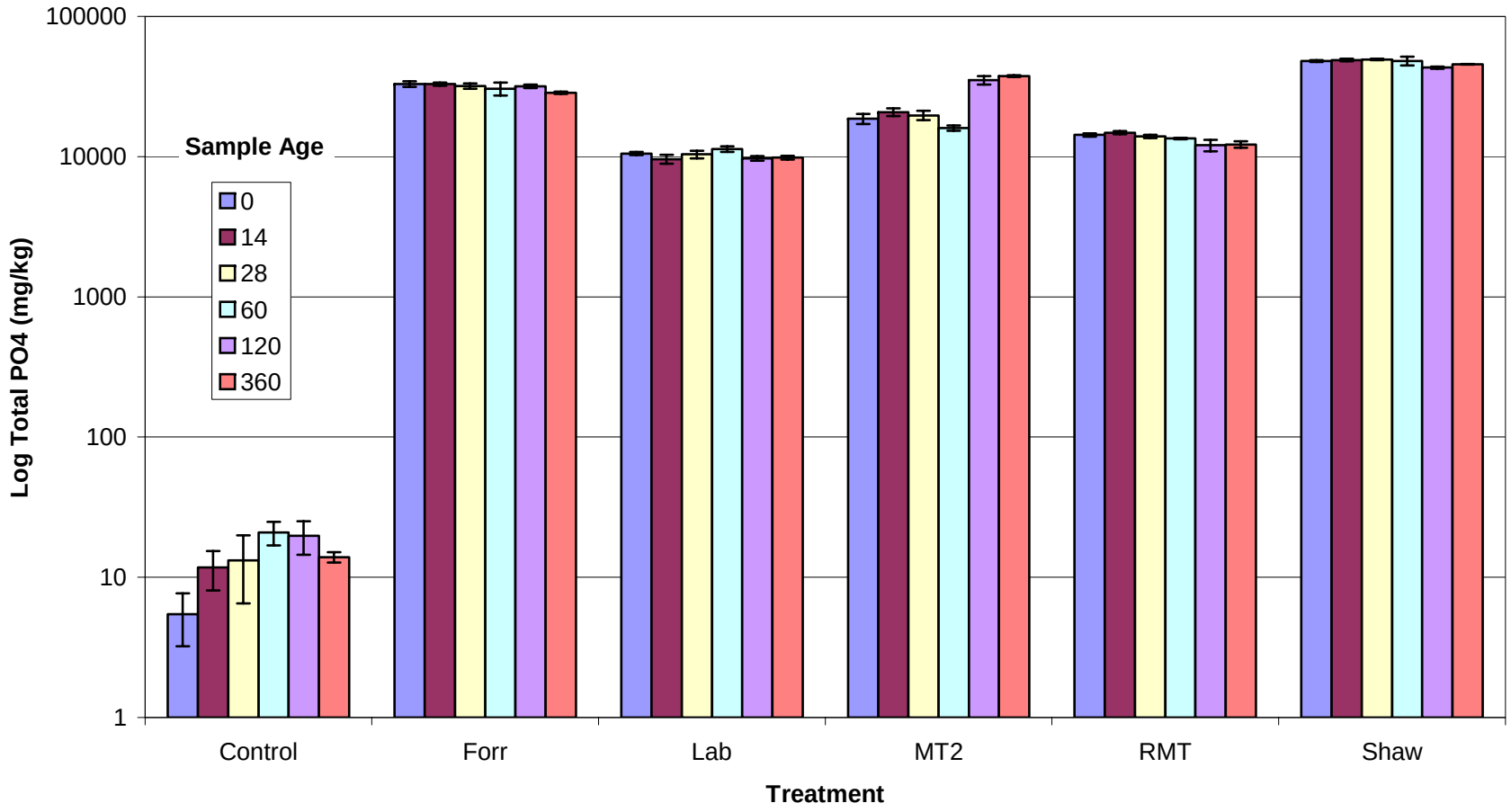


Figure 7-22. Total phosphate concentrations (mg/kg - log scale).

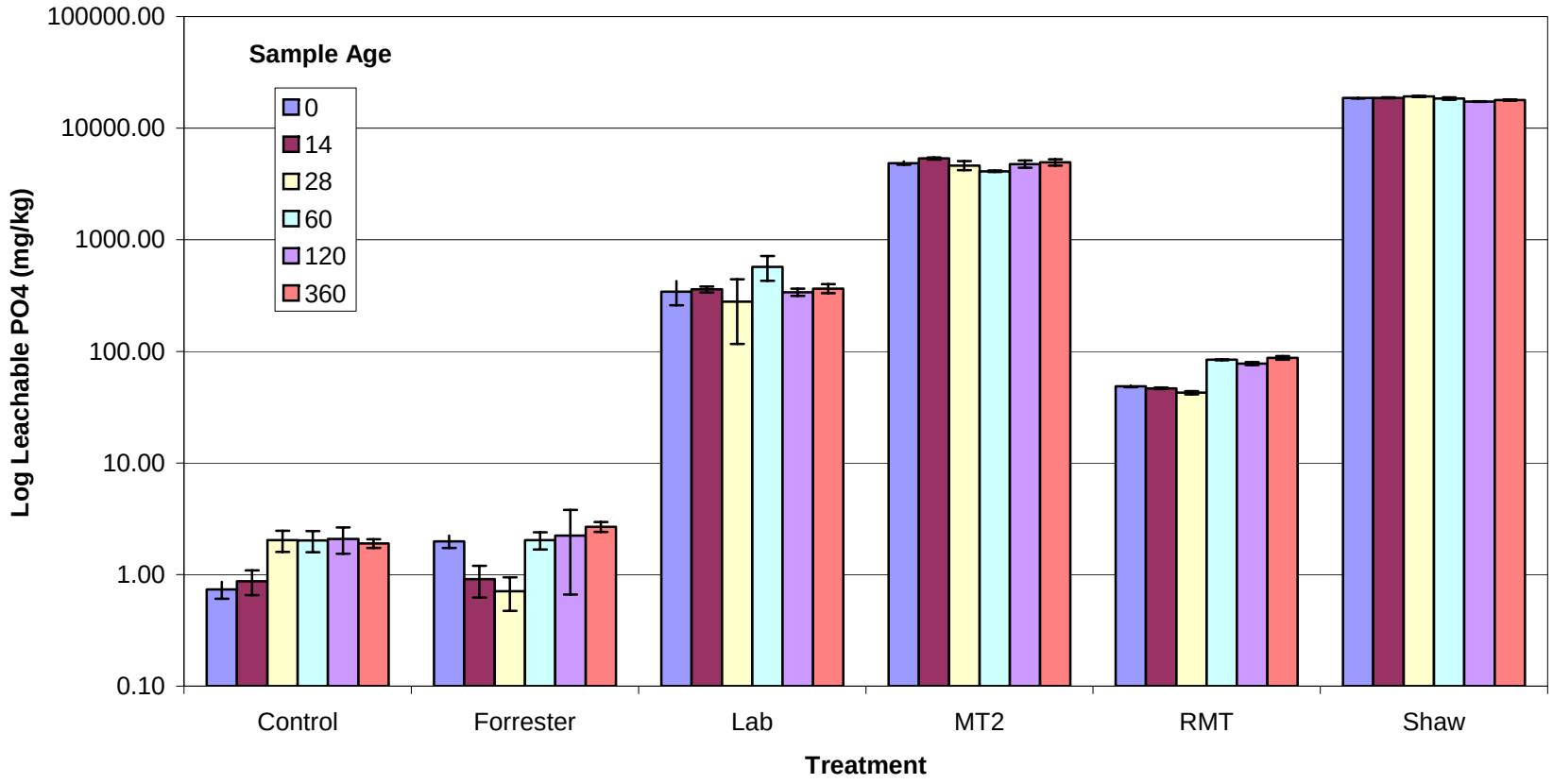


Figure 7-23. Leachable phosphate concentrations (mg/kg - log scale).

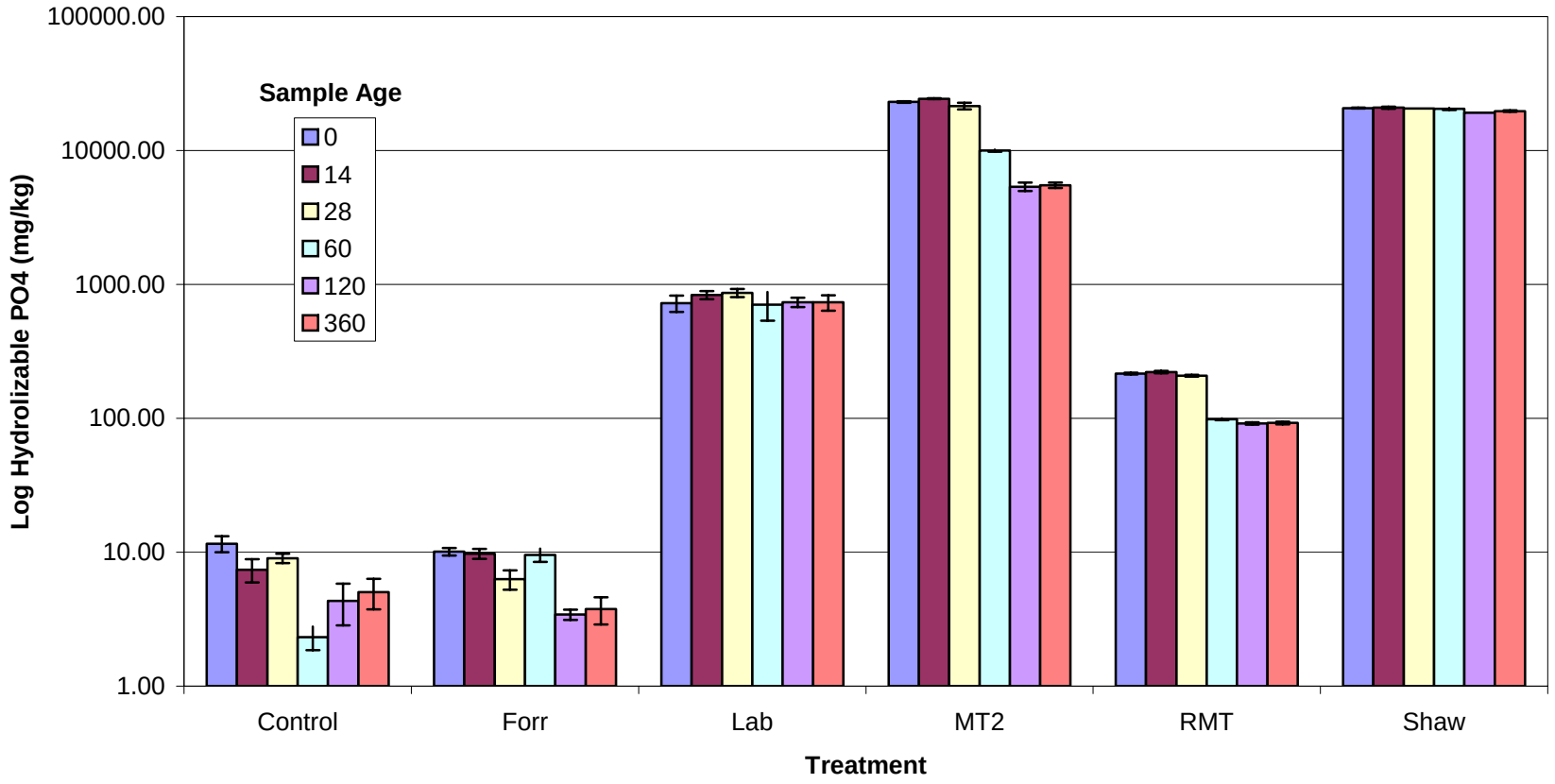


Figure 7-24. Hydrolyzable phosphate concentrations (mg/kg - log scale).

7.2 Physical Test Results

The average baseline physical test data for the Camp Withycombe soil prior to treatment were provided in section 5.2.5. Samples of the control soil were also subjected to the same aging conditions as the vendor treated soil and their physical properties were examined. The results of these tests are presented below.

7.2.1 Cone Index (CI)

The average results of the CI test are shown in Figure 7-25. As discussed previously, the maximum scale as measured by the CI test is 750 psi. Figure 7-25 shows most of the data points above the scale for this test. Samples above the scale of the CI instrument were reported at >750. For the CI test, all vendor treated samples showed an increase in CI values above the control. In fact, all vendor treated soils had CI values >750 psi on the 0-day sampling except for MT^2. The MT^2 samples reached >750 psi CI value by the 14-day sampling event. Based on these results, it appeared that the samples quickly achieved strength development early during the curing process.

7.2.2 Unconfined Compressive Strength (UCS)

The results of the UCS tests for the baseline sample and the 28-day control and vendor treated samples are provided in Figure 7-26. This data appears to show a slight increase in strength in all of the vendor treatment samples when compared to the control and baseline samples. MT^2 had the highest UCS gain over the control sample (the average UCS of the MT^2 sample was 34 psi).

An ANOVA was conducted on the data using three classes (vendor treatment = 6 levels, sample age = 2 levels, and replicates = 3 levels). This analysis indicated that the vendors and cure times were statistically different at the 99.9 percent CL. The replicates were not statistically different.

The results of the Duncan multiple range tests indicated the following groupings:

The Duncan test indicated that the UCS for the control samples was statistically lower than the vendor-treated samples. In addition, the UCS of the MT^2- and Lab-treated soils were statistically different from the Forrester and Shaw treated soils, although, the UCS differences observed were very small.

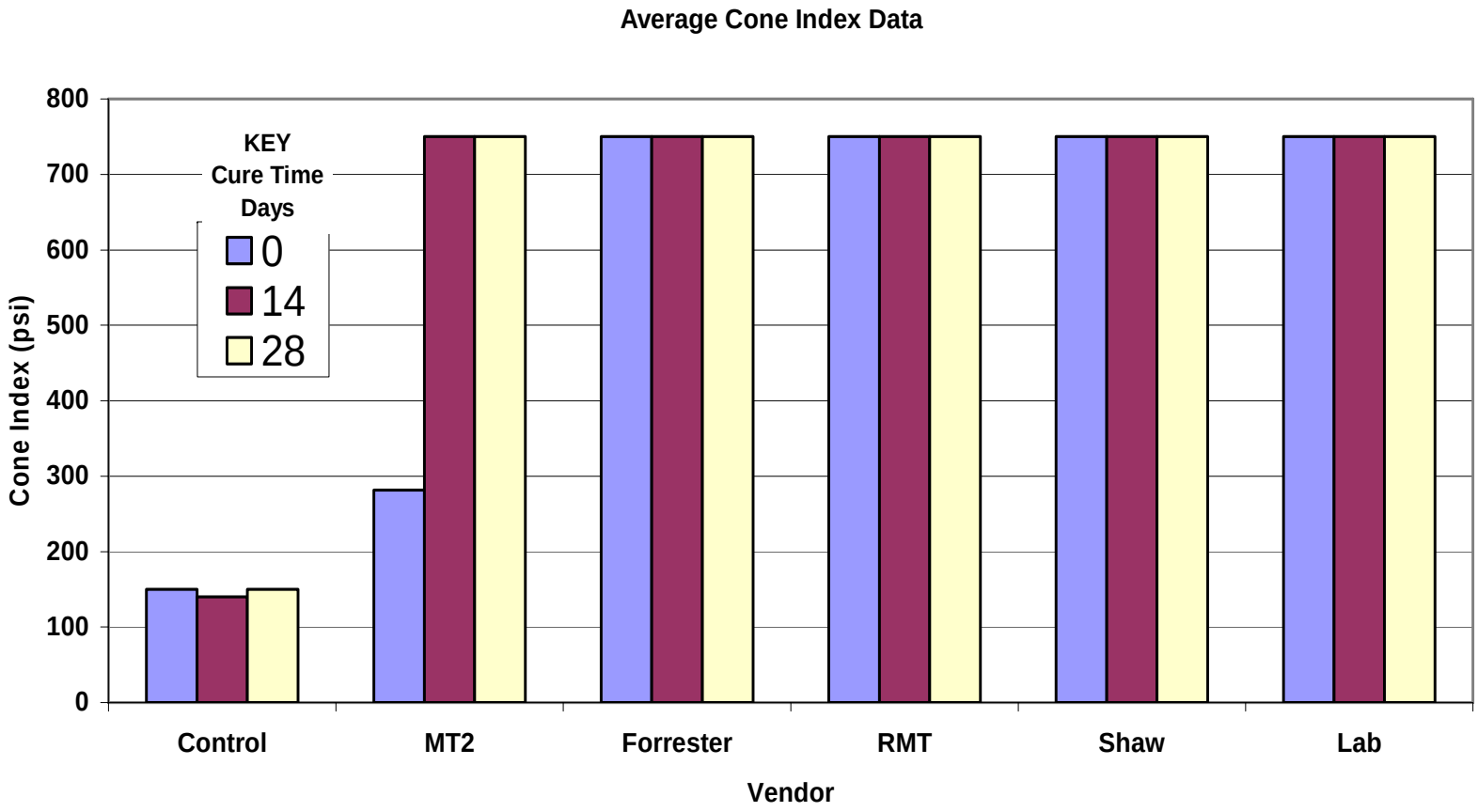


Figure 7-25. Average CI values.

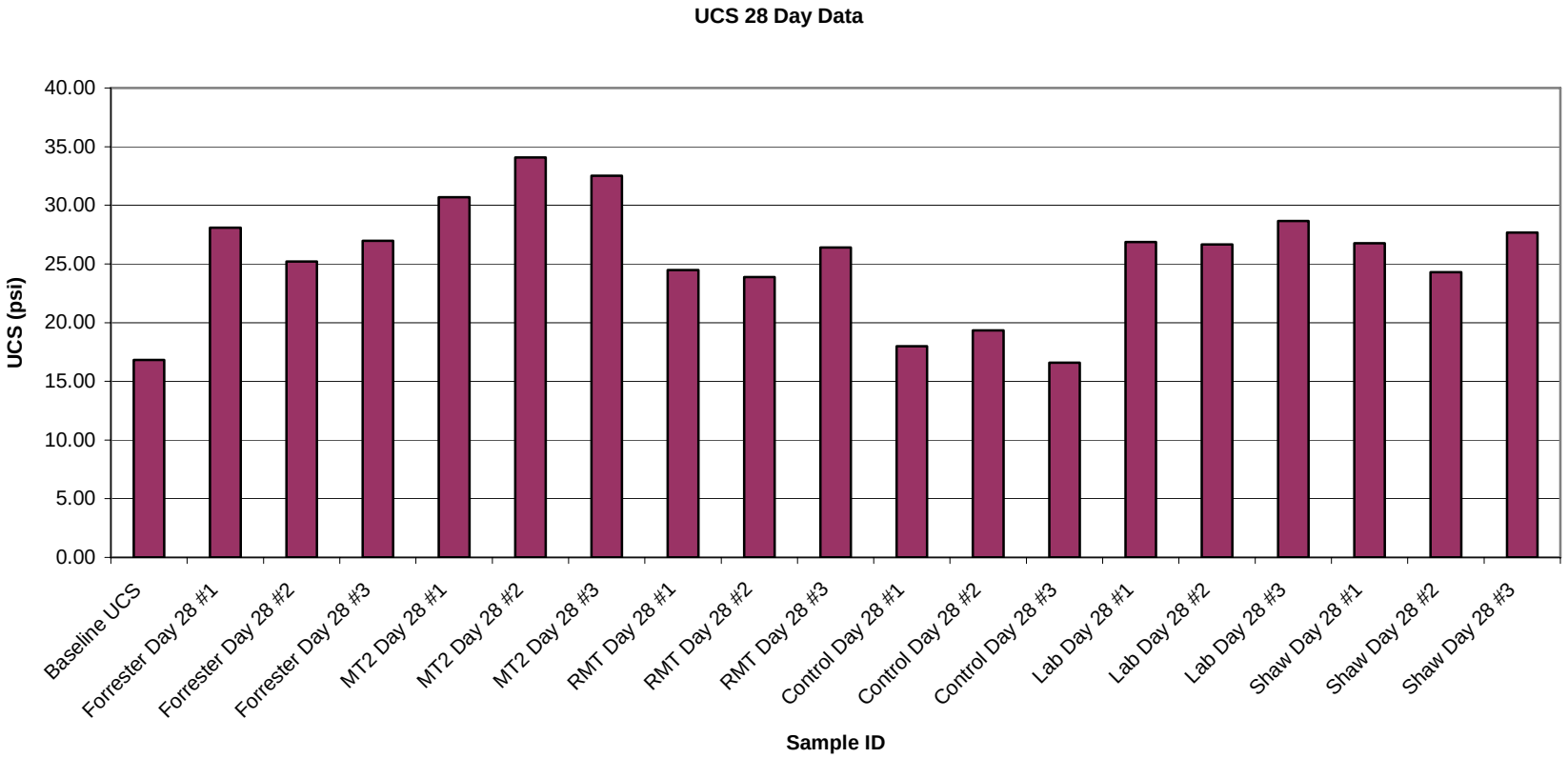


Figure 7-26. UCS for soil samples.

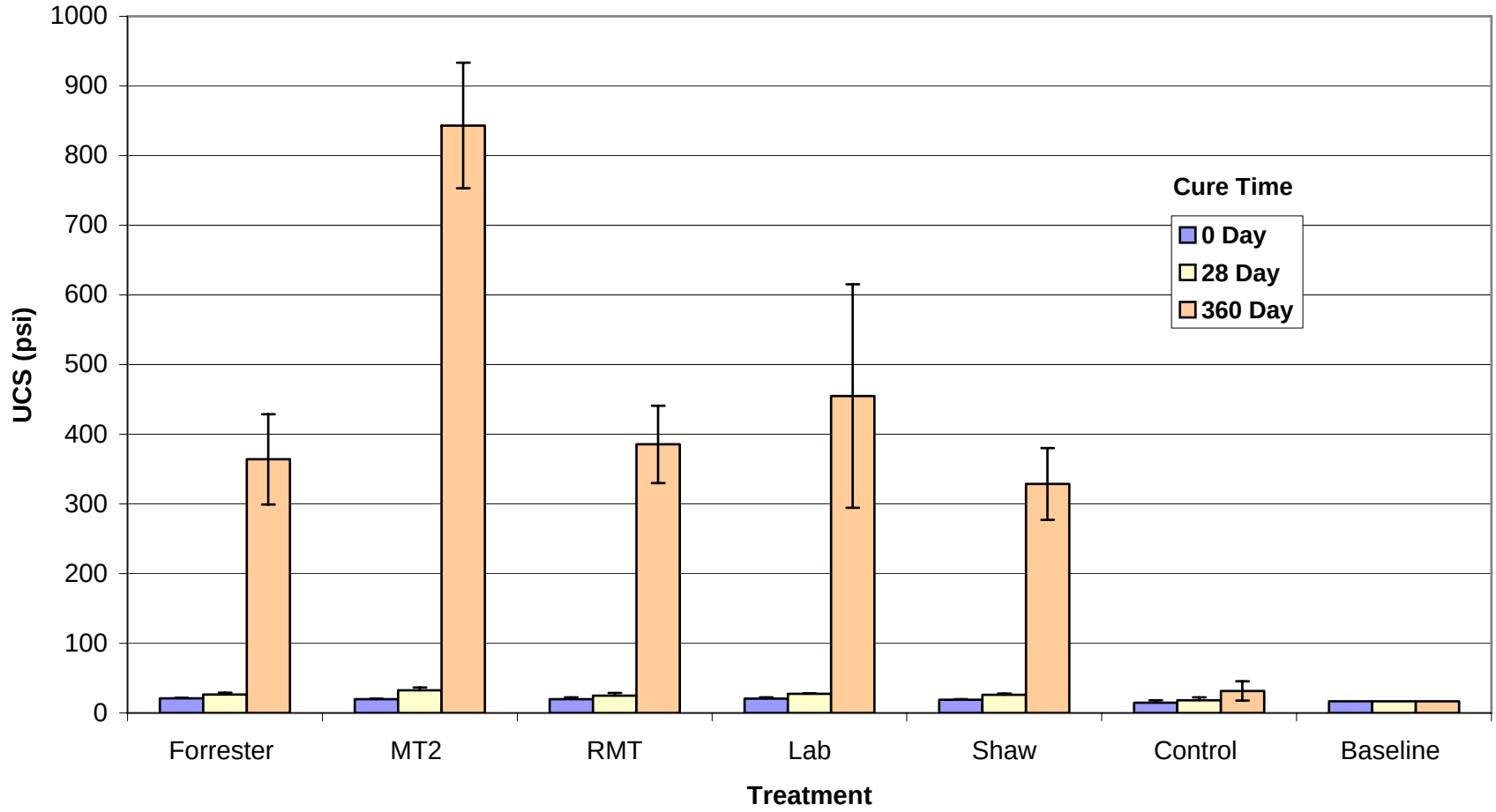


Figure 7-27. UCS for soil samples (0-, 28-, and 360-day results).

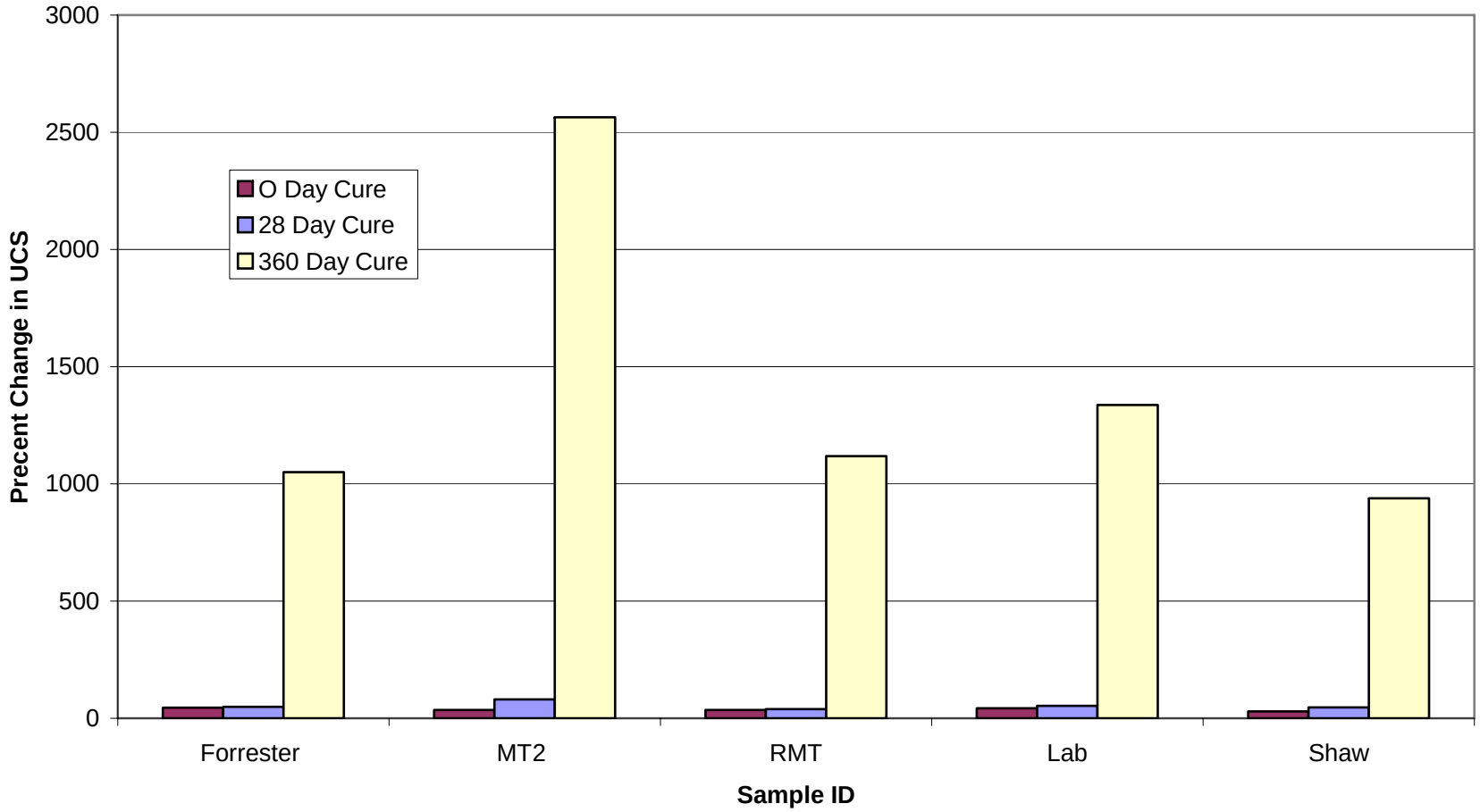


Figure 7-28. Change in UCS compared to control.

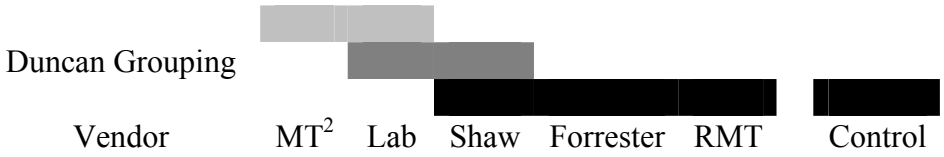
At MSU's discretion, an additional UCS data set was collected after 360 days of cure time. These data (averaged by replicate) are shown along with the 0- and 28-day control and vendor-treated soil data in Figure 7-27. After the extended cure time, a significant increase in UCS was measured in all of the vendor-treated soils. The control soil remained essentially constant over this period. MT^2-treated soils continued to have the highest UCS (>800 psi), followed by the Lab- (450 psi), RMT- (390 psi), Forrester- (360 psi), and Shaw- (320 psi) treated soils as previously determined by examination of the 28-day sample results. As seen in Figure 7-28, the increase in UCS after 360 days of curing resulted in increases of soil UCS of approximately 1000 to 2600 percent when compared to the control samples. The increase in UCS for the vendor samples may have resulted from either the binder that was added or as a result of the moisture and compaction applied to the samples. Although the UCS of the treated samples had substantially increased, they were still weak and crumbled easily.

7.2.3 Bulking

The changes in vendor-treated soil bulk density with respect to the control soil bulk density are presented in Figure 7-29. The densities used to determine these changes were the 0-, 28- and 360-day sample data averaged by replicate. As shown in this figure there was a slight decrease in the bulk density of the vendor treated soils as the soils aged. There was a 2 to 22 percent increase in bulk density of the treated soils when compared to the control.

An ANOVA was conducted on the data using three classes (vendor treatment = 6 levels, sample age = 3 levels, and replicates = 3 levels). This analysis indicated that the vendor treated samples were statistically different at the 99.9% CL. The sample cure times and replicates were not statistically different.

The results of the Duncan multiple range tests indicated the following groupings:



The Duncan tests indicated that the MT^2-treated soil bulk density was statistically higher than the Forrester- and RMT-treated soil bulk densities. The bulk densities of all of the vendor treated soils were statistically different from the control soil.

7.2.4 Permeability

The 28- and 360-day average permeability of the control and vendor treated soils is shown in Figure 7-30. These data indicated that there was little change in the vendor-treated soils average permeability when compared to the control. An ANOVA using three classes (vendor treatment = 6 levels, sample age = 2 levels, and replicates = 3 levels) indicated that there is no statistical difference between the permeability control and vendor-treated soils nor between the replicate samples at the 99.9 percent CL. As seen in Figure 7-30, all samples have a permeability of approximately 2.0E-06 cm/s.

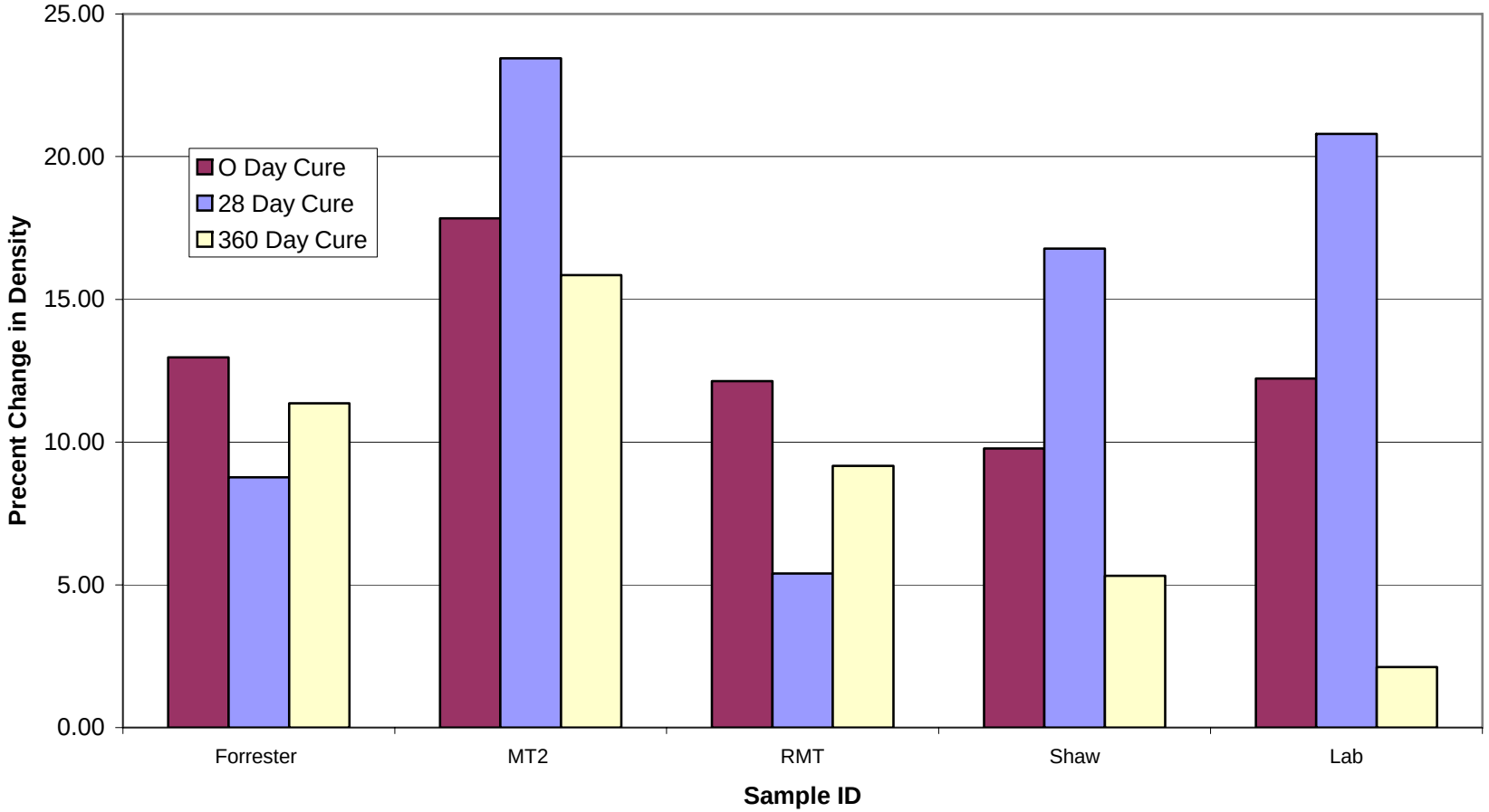


Figure 7-29. Bulking data.

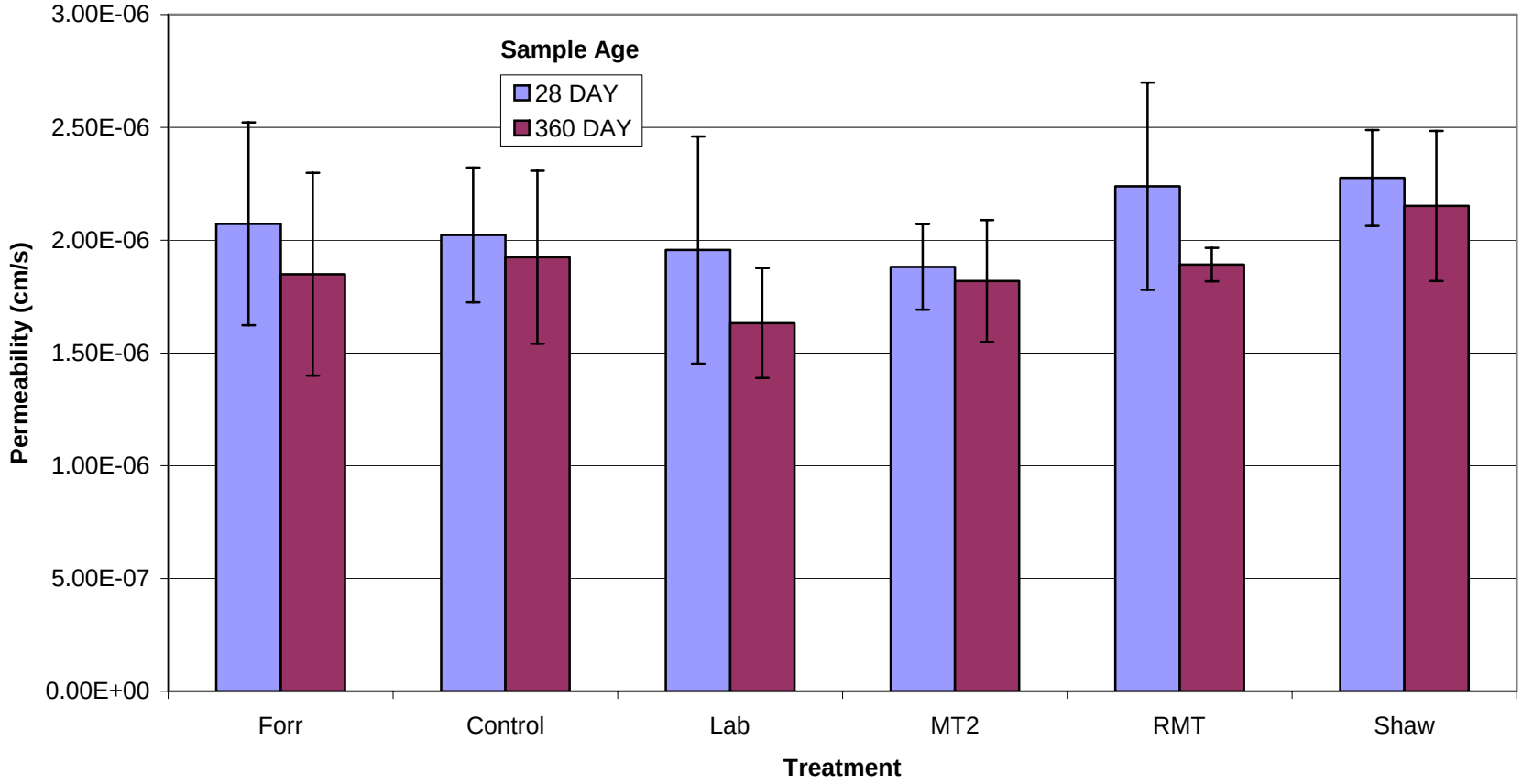


Figure 7-30. Permeability of the control and vendor-treated soils.

7.2.5 Particle Size Analysis

The average particle size distribution of the control and vendor-treated soils is shown in Figure 7-31. Based on Figure 7-31, there appears to be a very slight change in the particle size distribution of the vendor treated soils when compared to the control. The vendor treatments appear to have caused a slight increase in larger particles (in approximately the 1.0 to 10.0 mm range) and a decrease in the particles in the 0.01 to 1.0 mm range. Based on this data the control and vendor treated soils are classified as silty clays according to ASTM D 2487-93, as described in the Methods and Materials section of this report.

7.3 Other Tests Results

7.3.1 MICROTOX® Test

The results of the MICROTOX® tests (averaged by replicate) are presented in Figure 7-32 for the control and treated soils. From this figure it is difficult to observe any trends in the data. An ANOVA using three classes (vendor treatments = 6 levels, sample age = 6 levels, and replicates = 3 levels) indicated that there were no statistical differences between the vendor treated samples and the control or cure times at the 99.9 percent CL. This indicated that the vendor treatments did not affect biological growth negatively or positively for the microbial species used in the MICROTOX® test.

7.3.2 Reduction of Lead Bioavailability Using Plants

Evaluating the vendor treatment's impact on the plant uptake of lead was a secondary performance objective. A comparison between the control and treated soils using hyper-accumulator plant species was made to evaluate whether any change in the plant metal uptake had occurred as a result of the application of the vendor amendments.

For this portion of the study, the treated soils were allowed to age for a minimum of 28 days after treatment. Brassica juncea seeds and Pisum Sativum seeds were sown in pots of the treated and control soils. Additionally, an uncontaminated topsoil control sample was included to monitor plant growth with respect to the Camp Withycombe control and treated samples. The original plan was to grow the plants until seed germination, but several of the plants were stressed and began to die after 30 days. The plants were harvested at the end of the 30-day period.

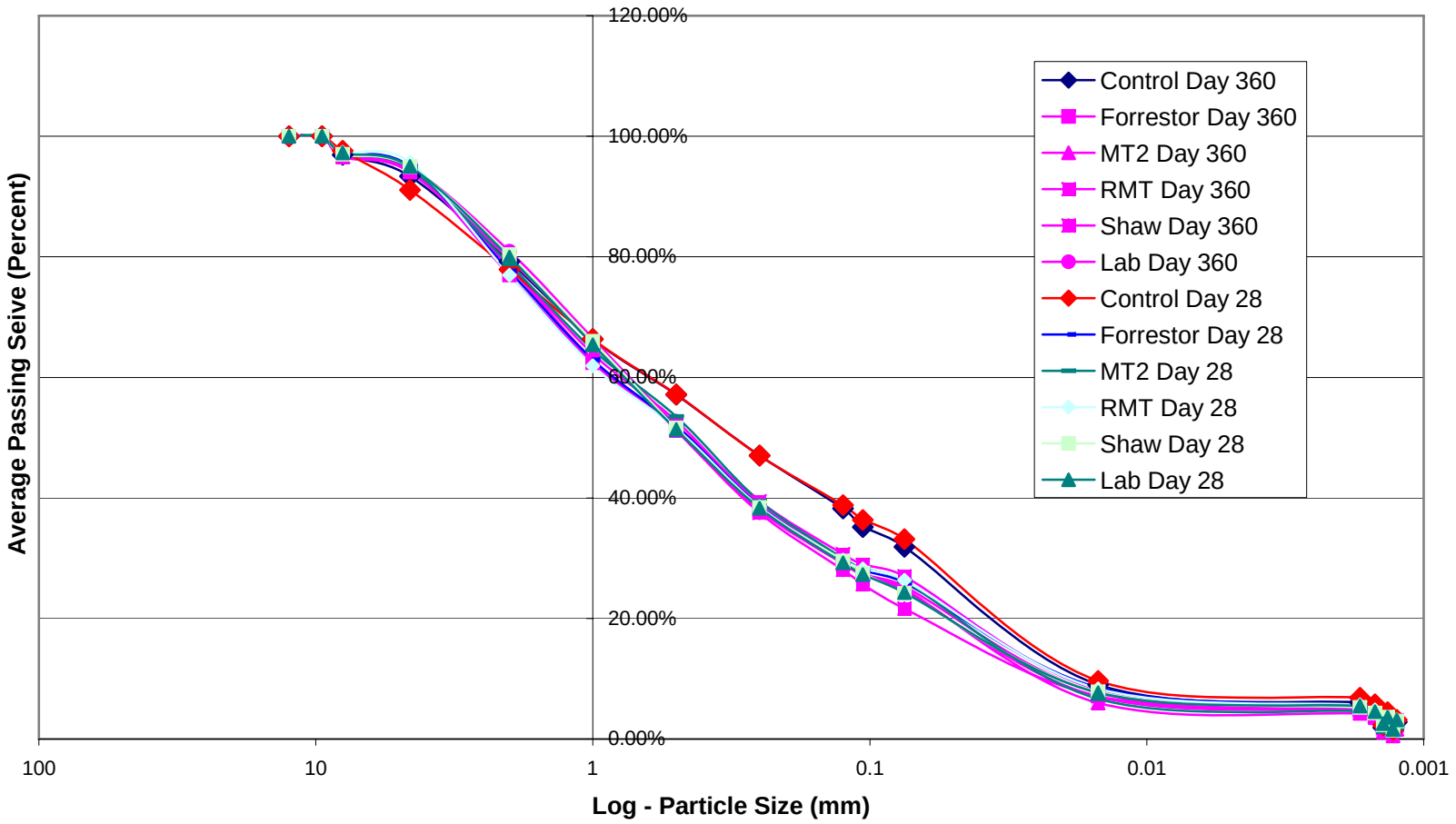


Figure 7-31. Particle size distribution of the control and vendor-treated soils.

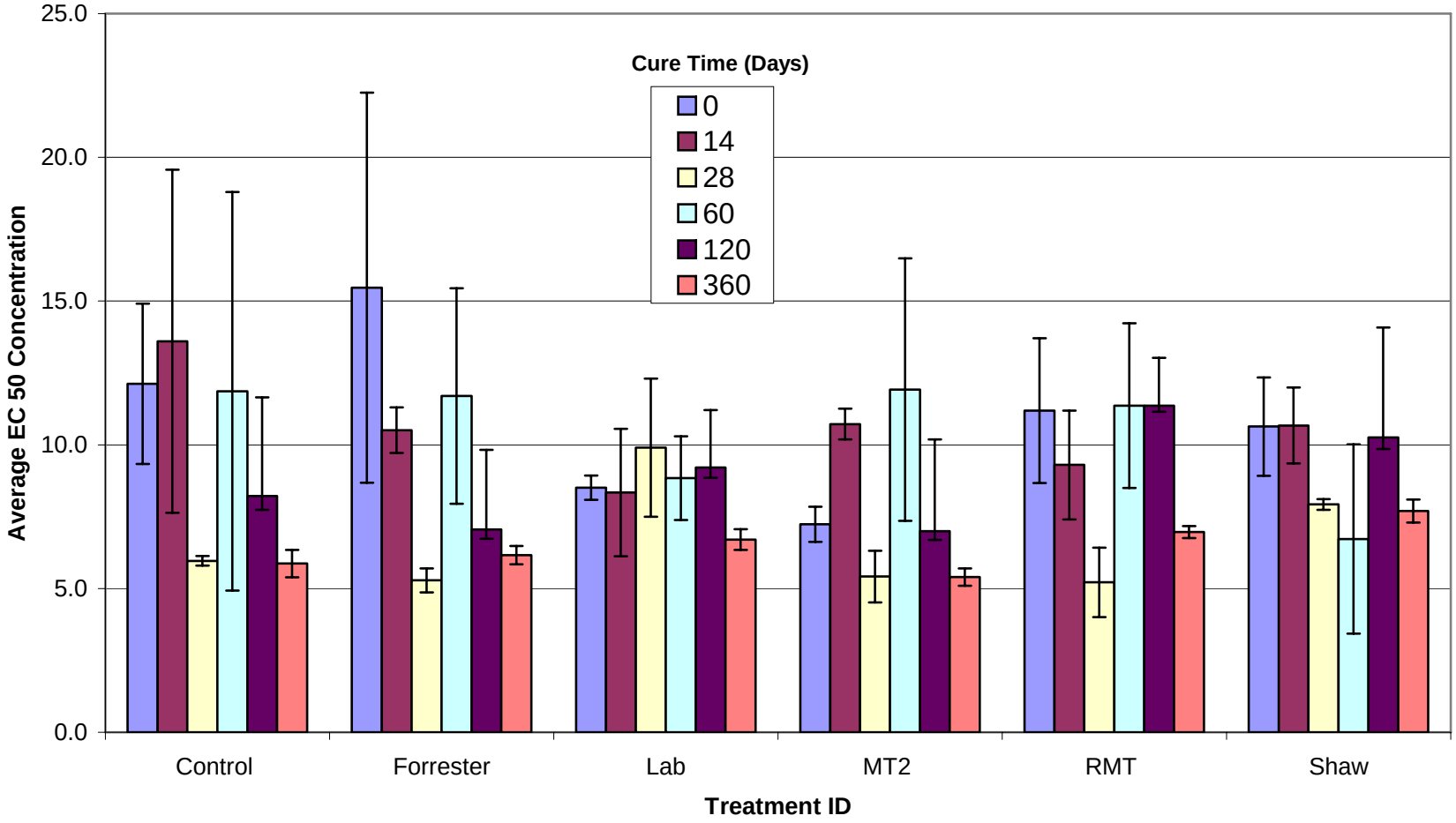
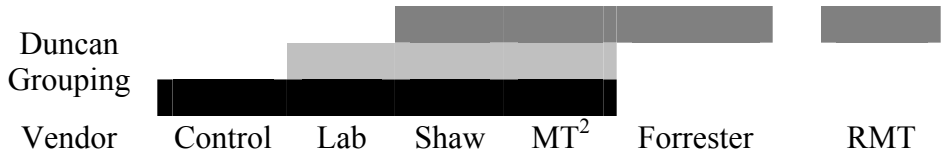


Figure 7-32. MICROTOX® Results for the control and vendor-treated soils.

The results of this plant growth study and plant lead concentration data are provided in Figure 7-33. Lead uptake in both plant species in the control soils was approximately the same (870 mg/kg). Data from the Pisum Sativum indicated a substantial reduction in plant lead uptake for most vendor-treated soils when compared to the control. The RMT-treated soil was the one exception where lead uptake reduction was less pronounced. The Brassica Juncea plant lead uptake data were mixed. Lead reductions were observed in the Forrester- and MT^2-treated soils. The Shaw-treated soil results indicated essentially no reduction of lead uptake. The Lab-treated soil indicated an approximate 100 percent increase in lead uptake. The Brassica Juncea sown in the RMT-treated soil never emerged. The cause for the failure of the Brassica Juncea to establish in the RMT-treated soil could not be determined based on available data. Both plants thrived in the topsoil control samples, so the failure of the Brassica Juncea in the RMT-treated soil may be due to the amendments added to the soil or their effects on contaminant uptake by the germinating plant. Figure 7-34 presents the data at the percent lead immobilized (on a normalized dry raw soil basis). The Pisum Sativum lead uptake results in this figure indicate that over 85 percent of the lead was immobilized for all vendor treated soils except RMT. The range of lead immobilization based on the Brassica Juncea lead uptake results varied from 6 to 64 percent except for the Lab-treated sample. Lead mobilization increased 100 percent in the Lab-treated sample.

An ANOVA was conducted on the plant data set (excluding the top soil data) using three classes (vendor treatment = 6 levels, plant type= 2 levels, and replicates = 9 levels). This analysis indicated that the vendor treatments and plant types were statistically different at the 99.9 percent CL.

The results of the Duncan multiple range tests indicated the following groupings:



The Duncan tests indicated that the RMT-treated soil lead uptake was statistically different from the control and other vendor-treated soils. Additionally, the Forrester-treated soil lead uptake was different from the control soil. No statistically significant differences were found between the control soil lead uptake characteristics and the Lab-, Shaw-, and MT^2-treated soil lead uptake characteristics.

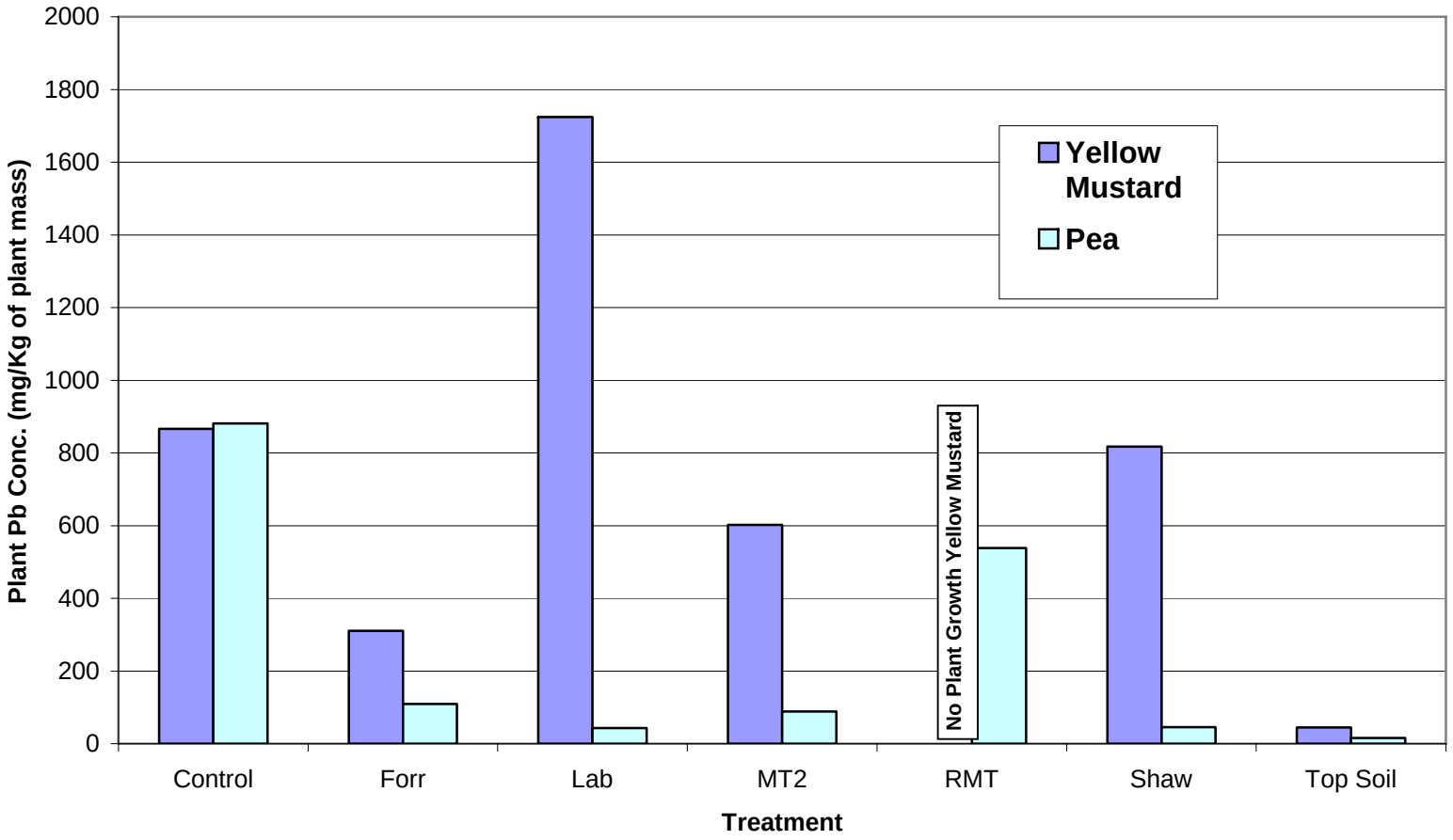


Figure 7-33. Lead concentration in plant tissue, mg/kg dry weight.

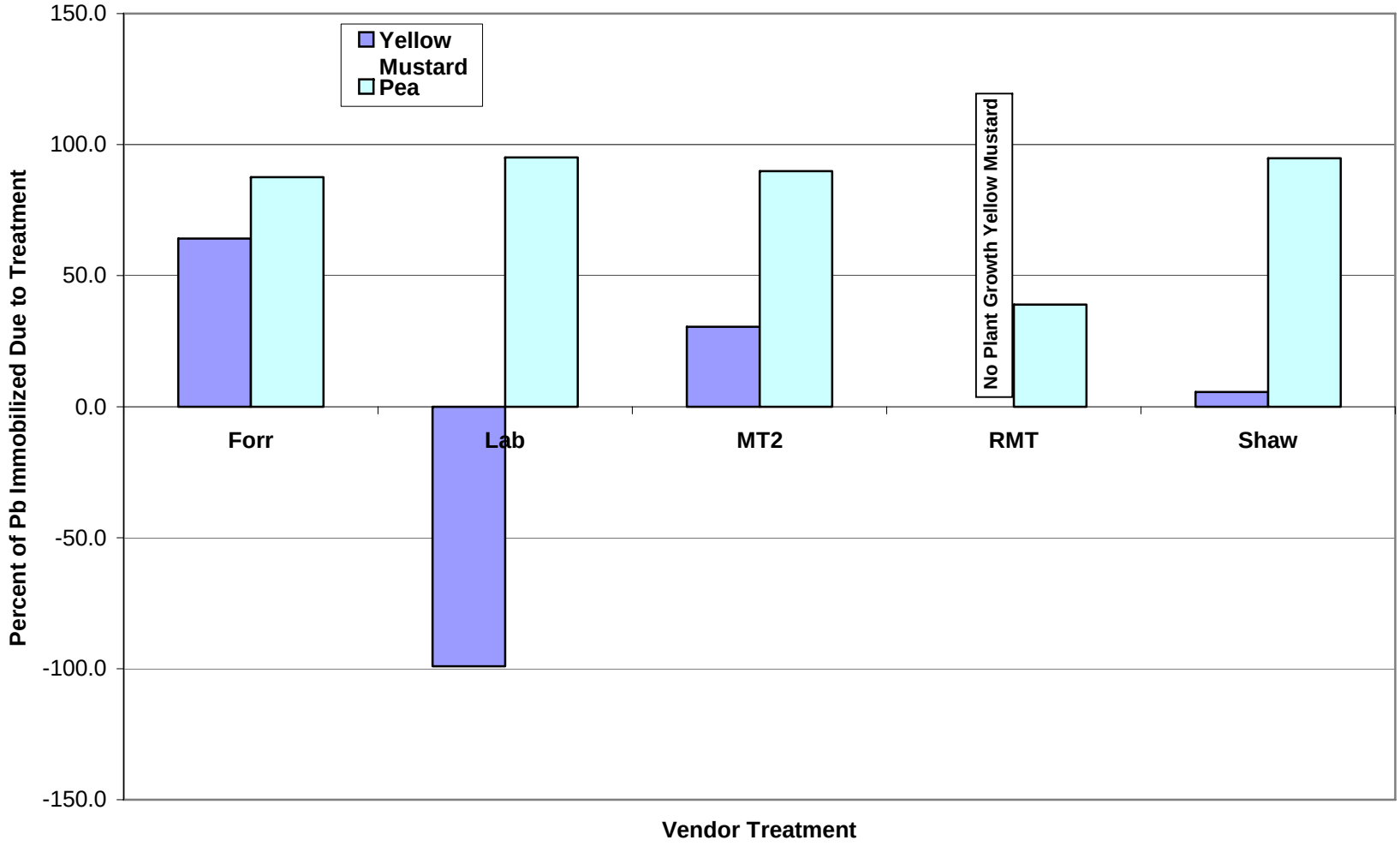


Figure 7-34. Lead concentrations in plant tissue.

8.0 CONCLUSIONS AND RECOMMENDATIONS

8.1 Conclusions

The data collected was used to evaluate the objectives of the treatability study specified in section 3. The performance objectives against which the vendor treatments were evaluated are presented in Table 3-1. The conclusions with respect to each subordinate objective are discussed in the following subsections.

8.1.1 Soluble Lead Mobility Reduction

A substantial reduction of lead mobility was observed in the TCLP analyses. The TCLP results for most of the vendor treated samples were below 5.0 mg/L except for the 120- and 360-day Lab-treated samples, one 120-day RMT-treated sample, and one 60-day and all 120-day MT^2-treated samples. When compared to the control average TCLP results (318 mg/L), the vendor treatments generally resulted in a greater than 98.5 percent reduction in leachable lead from the soil. The TCLP lead concentration data for the Forrester- and Lab-treated soils indicated a slight increase in TCLP lead concentrations as the treated soils aged. No changes in TCLP lead concentrations were observed in the control or the MT^{2-}, RMT-, and Shaw-treated soil over the 360-day monitoring period.

The SPLP lead concentration results indicate that the vendor treatments had varying effects on reducing the SPLP lead concentrations (see section 7.1.4). There was no apparent pattern in the SPLP variations associated with aging of the treated soils as seen in some of the TCLP results.

The SET lead concentration results indicated a shift in lead concentrations from the more soluble fractions in the control (fractions No. 1 through 3) to the less soluble fractions in the treated soils (fractions No. 4 and 5). This data indicates that the phosphate treatments have resulted in a reduction in the solubility characteristics of the lead in the soil.

Although these tests do not definitively determine whether a pyromorphite compound had been formed, the results allowed the inference of relatively insoluble complex formation. The varying SPLP results and the trends in some of the TCLP results continue to call the long-term stability of the treated lead into question. A recent laboratory study investigating the benefits of using phosphate amendments to manage lead in soils on active small arms ranges (Larson et al) indicated that there appears to be a soil dependence on the long-term stability of the stabilization process. This study related the soil particle size and its capacity to establish bonds with the metal ions to the phosphate stabilization efficiency with fine-grained soils, clays and silts, yielding the best performance. Additionally, the amount and type of organic content in the soil, as well as the presence of other competing salts (carbonates, sulfides, sulfates, etc.) can have an affect on the metals species formation. The factors affecting preferential metals chelation or adsorption (organic content, inorganic salts, biological activity, etc.) and their effects on long-term stability of the metals species require further study to accurately predict soil amendment performance results.

8.1.2 Ease of Use

Proposals submitted by the vendors, with the exception of Shaw, for the conduct of the field demonstration were similar in methods of application. Typically, the amendments were topically applied and mechanically mixed into the soil. The Shaw application method involved mixing the amendments with water and injecting or flooding the treatment area. This application method, especially on the hillside at Camp Withycombe, may potentially create a runoff and/or leachate issue. The vendors' estimated costs for treating the soil were comparable, with the exception of Shaw, with amendment cost being the primary variable. Shaw capital costs were higher to accommodate the equipment requirements and on-site setup and operation costs of the mixing and injection equipment.

8.1.3 Human Health Risk Reduction

Bioavailability reduction was evaluated through comparison between the untreated control and treated soil PBET results. The PBET lead concentrations in the treated samples indicated that a reduction in bioaccessible lead occurred when compared to the control data. All treated soils exhibited significant variations in PBET lead concentration results over the monitoring period. These changes in lead concentrations likely resulted from changes in lead species stability over time since there appeared to be a general pattern of decreasing lead concentration during the first 28 days followed by an increase in lead concentration through the remainder of the monitoring period.

The results of the IEUBK model analysis indicated that 93.9 to 99.5 percent of the population exposed to the treated soils would have PbB greater than the 10 µg/dL. The Camp Withycombe average soil lead concentration was 11,700 mg/kg. The vendor treatments were not able to reduce the bioaccessibility of the high concentrations of lead in the Camp Withycombe soils enough to reduce the exposure risk presented at the site. Soil lead concentration will be a limiting factor in the use of phosphate-based amendments for in situ stabilization.

These results were discussed with the Oregon Military Department (OMD), ODOT, and ODEQ in February 2005. The general consensus was that in situ treatment would not be an option for the Camp Withycombe site.

8.1.4 Mobility Impact to Other Existing Metal Contaminants

Four of the vendor treatments (Lab, MT^2, RMT, and Shaw) generally had little to no effect on the COC TCLP concentrations, excluding lead. Forrester treated soils generally had lower TCLP concentrations for arsenic, copper, nickel, and zinc. Antimony was the only COC that was not reduced by the Forrester treatment. In general, excluding lead and copper, the TCLP COC concentrations were between 0.01 and 1.0 mg/L. Generally, the COC TCLP concentrations met the performance criteria in Table 3-1 with the exception of the objective criteria for arsenic. All vendors met the arsenic threshold criteria of 5 mg/L, but an objective level of 4 µg/L was identified for arsenic. None of the vendor treatments were able to meet this

criterion. Discussions with OMD, ODOT, and ODEQ indicated that more stringent criteria may be identified for in situ cleanup dependent upon the results of an ecological risk assessment. These criteria were not available for this phase of the assessment.

All vendor treatment soils leached substantial quantities of phosphate except for the Forrester treated soils. Regulatory limits for phosphate in storm water runoff or groundwater are typically site specific. Discussions with OMD, ODOT, and ODEQ determined that discharge limits for phosphate have not been investigated for the Camp Withycombe site. Further investigations of Camp Withycombe site specific requirements would be necessary; however, the general consensus was that minimizing amendment mobilization away from the treated soils would be desirable.

8.1.5 Impact of Technology on Soil Toxicity

The results of the MICROTOX® tests indicated that there were no differences in soil toxicity between the vendor treated soils and the control soil. This indicated that the vendor treatments did not affect biological growth negatively or positively for the microbial species used in the MICROTOX® test.

8.1.6 Impact of Applying Amendments upon Soil Properties

A significant increase in UCS was measured in all of the vendor treated soils. MT^2-treated soils had the highest UCS (>800 psi), followed by the Lab- (450 psi), RMT- (390 psi), Forrester- (360 psi), and Shaw- (320 psi) treated soils. These increases in UCS range from approximately 1000 to 2600 percent after 360 days of curing when compared to the control samples. The increase in USC for the vendor samples may have resulted from either the binder that was added or as a result of the moisture and compaction applied to the samples. Although the UCS of the treated samples had substantially increased, they were still weak and crumbled easily.

Soil bulk density of the vendor treated soils increased from 2 to 22 percent with respect to the control soil bulk density. There was little change in the vendor treated soils average permeability when compared to the control. Minor changes occurred in the particle size distributions of the vendor treated soils, but they were not enough to significantly change the physical properties of the soil.

This data was discussed with OMD, ODOT, and ODEQ. ODOT had been particularly interested in physical changes to the soil. The data discussed did not appear to present any potential construction issues with the planned highway.

8.1.7 Reduction to Lead Bioavailability Using Plants

The Pisum Sativum lead uptake data indicated a substantial reduction in plant lead uptake for most vendor-treated soils when compared to the control. The one exception was the RMT-treated soil where lead uptake reduction was less pronounced. The Brassica Juncea plant lead uptake data was mixed with plant lead concentration reductions in the Forrester- and MT2-treated soils, plant lead concentration increases in the Lab-treated soil, and essentially no change

occurred in plant lead concentration in the Shaw-treated soil. The Brassica Juncea sown in the RMT-treated soil never emerged. The cause for the failure of the Brassica Juncea to establish in the RMT-treated soil could not be determined based on available data. Both plants thrived in the topsoil control samples, so the failure of the Brassica Juncea in the RMT-treated soil may have been due to the amendments added to the soil or their effects on contaminant uptake by the germinating plant.

In general, the plant data indicated that the lead uptake can vary substantially according to the type of phosphate amendment. The lead uptake by plants can be expected to be influenced by a combination of the site-specific soil characteristics (i.e., mineral and organic constituents, biota, etc.), type of amendment(s) used, and the type and variety of local plants in the treated areas. Further study is needed to understand the effects of these factors on lead stability in treated soils.

This data was discussed with OMD, ODOT, and ODEQ. ODEQ recognized that the hyper-accumulator plant species used in the lab study was intended to identify general trends in plant bioavailability. Prior to approval for use of phosphate treatment as a remedial corrective action method, a site-specific ecological assessment would have to be performed to determine the effects of the stabilized lead.

8.1.8 Ability to Meet Regulatory Cleanup Standards for Land Disposal

All of the vendor-treated soils failed to meet the 0.75 mg/L TCLP UTS performance criteria with the exception of the Forrester 0-, 14-, 28-, 60-, and 120-day samples and the RMT 360-day sample. With the trends towards increasing TCLP lead concentrations observed in the data, a determination supporting long-term stability could not be made.

This data was discussed with OMD, ODOT, and ODEQ. The 360-day Forrester data was not available at the time of this discussion and the existing data met the performance criteria. At this point OMD, ODOT, and ODEQ supported field testing of the Forrester soil amendment; however, the 360-day data and a subsequent 505-day sample analysis indicated the treatment was not able to maintain the lead stability within the UTS performance criteria.

8.2 Recommendations

Field demonstration of the phosphate-based lead stabilization as an in situ treatment method is not recommended at Camp Withycombe for the following reasons:

- Human health risk reduction performance criteria were not met by any of the vendor amendments.

- Long-term stability of the lead in the soil is questionable based on the data collected.

- The plant lead uptake study indicated a wide variability in lead availability. The variability is suspected to be the result of site-specific chemical and biological reactions, as well as plant species' metal uptake characteristics, that may limit the use of the technology for in situ applications.

Treatment and on-site disposal under the road bed of the planned highway instead of in situ treatement was considered potentially to be an option when the data was discussed with the OMD, ODOT, and ODEQ officials. This option minimized the potential for human and ecological exposure. Long-term stability is the predominant criterion required to support this remedial option. The initial data supported Forrester in its lead stabilization treatment with TCLP lead results meeting UTS treatment criteria during the 0- through 120-day curing periods; however, the 360- and 505-day Forrester TCLP data failed to meet established treatment criterion. As observed in Figure 7-9, the lead TCLP concentration increased to 2.0 mg/L at 360 days and then decreased to 1.1 mg/L at 505 days. The significance of this bump in TCLP concentration and whether there is a trend towards reduced stability in the Forrester-treated soil cannot be determined based on the available data. ATC recommends that further research be conducted to investigate biogeochemical, microbial, and hydrological influences on the metals speciation and stabilization process. A better understanding of these factors is needed in order to predict the applicability and performance of phosphate amendments as a means of stabilizing metals on site.

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APPENDIX A. LITERATURE REVIEW

Subject: Phosphate Treatment of Lead Contaminated Soil

A.1 Soil

"Soil may be defined as a natural body, synthesized in profile form from a variable mixture of broken and weathered minerals and decaying organic matter, which covers the earth in a thin layer and which supplies, when containing the proper amounts of air and water, mechanical support and, in part, sustenance for plants" (ref A1). The residual products that result from weathering of rocks and minerals (ref A2) form horizontal layers of soil.

Regolith is the unconsolidated material found on underlying rocks or "bedrock". It may have been produced by the weathering of underlying rock, or it may have been transported by wind, water, or ice and deposited on the bedrock. The upper 3 to 6 feet of regolith is different from the soil sub layer as a result of a relatively high organic matter, an abundance of roots, and intense weathering. This layer is considered to be "mineral soil," the layer where most plants grow. The surface soil contains a zone of maximum organic accumulation. Subsoil characteristics are determined by the forces that form the soil and the substratum (or parent material) which may be more or less weathered (ref A1).

Soils consist of three phases: a solid phase (50 percent), a liquid phase (25 percent), and a gas phase (25 percent). Mineral soils contain about 50 percent pore space that contains a mixture of air and water. Subsoils are usually more compact, lower in organic matter, and have a higher percentage of small pores (ref A1). More than 90 percent of the solid components of soil are composed of inorganic matter. Inorganic matter includes primary and secondary minerals, ranging in size from clay-sized colloids (<2 μm or 0.002 mm) to gravel (>2 mm) and rocks (ref A3). The larger mineral fragments are usually imbedded in and coated with colloidal and other materials. The mineral particle size will influence the properties of soils. When large mineral particles are predominant, the soil has characteristics of either gravel or sand. When mineral colloids are predominant, the soil is more likely to have clay-like properties (ref A1 and A3).

A primary mineral, such as quartz or feldspar, is more or less unchanged in composition from its original rock form. Most have not been altered (except for size) since they were deposited and crystallized from molten lava. Primary minerals are located in the coarser portions of soil such as sand (particle diameter of 0.05 to 2 mm) and silt (particle diameter of 0.002 to 0.05mm). Secondary minerals, such as silicates and iron oxides, are formed by the weathering of less resistant minerals. These secondary minerals are primarily found in the fine materials of soil, especially the clay portion, but may also be found in the silt fraction. The silt fraction is composed of aluminosilicate minerals, oxides, amorphous materials, sulfur, and carbonate minerals. Table A-1 presents a list of primary and secondary minerals found in soils (ref A3).

TABLE A-1. COMMON PRIMARY AND SECONDARY MINERALS IN SOILS

Primary Minerals		Secondary Minerals	
Name	**Chemical Formula**	**Name**	**Chemical Formula**
Quartz	SiO_2	Clay Minerals	
Muscovite	$KAl_2(AlSi_3O_{10})(OH)_2$	Kaolinite	$Si_4Al_4O_{10}(OH)_8$
Biotite	$K(Mg,Fe)_3(AlSi_3O_{10})(OH)_2$	Montmorillonite	$M_x(Al,Fe^{2+},Mg)_4Si_8O_{20}(OH)_4$ M=interlayer metal cation
Feldspars		Vermiculite	$(Al,Mg,Fe^{3+})_4(Si,Al)_8O_{20}(OH)_4$
Orthoclase	$KAlSi_3O_8$	Chlorite	$\{MAl(OH)_6\}(Al,Mg)_4(Si,Al)_8O_{20}(OH,F)_4$
Microcline	$KAlSi_3O_8$		
Albite	$NaAlSi_3O_8$		
Amphiboles		Allophane	$Si_3Al_4O_{12} \cdot nH_2O$
Tremolite	$Ca_2Mg_5Si_8O_{22}(OH)_2$	Imogolite	$Si_2A_4O_{10} \cdot 5H_2O$
Pyroxenes		Goethite	FeOOH
Enstatite	$MgSi_3$	Hematite	α-Fe_2O_3
Diopside	$CaMg(Si_2O_6)$	Maghemite	Υ-Fe_2O_3
Rhodomite	$MnSiO_3$	Ferrihydrite	$Fe_{10}O_{15} \cdot 9H_2O$
Olivine	$(Mg,Fe)_2SiO_4$	Boehmite	Υ-AlOOH
Epidote	$Ca_2(Al,Fe)_3Si_3O_{12}(OH)$	Gibbsite	$Al(OH)_3$
Tourmaline	$(Na,Ca)(Al,Fe^{3+},LiMg)_3Al_2$	Pyrolusite	β-MnO_2
	$6(BO_3)_3(Si_6O_{18})(OH)_4$	Birnessite	δ-MnO_2
Zircon	$ZrSiO_4$	Dolomite	$CaMg(CO_3)_2$
Rutile	TiO_2	Calcite	$CaCO_3$
		Gypsum	$CaSO_4 \cdot 2H_2O$

Source: Sparks, 1995.

The remainder of the solid portion of soil is composed of soil organic matter (SOM). SOM is the soil fraction that is comprised of partially decayed and partially re-synthesized plant and animal residues. SOM consists of two parts: original tissue (and its partially decomposed equivalents) and humus (ref A1). The amount of SOM in soil depends on five factors that determine the equilibrium level of SOM: time, climate, vegetation, parent material, and topography. The SOM of soils range from 0.5 to 5 percent of the weight of mineral soils, up to 100 percent for organic soils. SOM represents only 3 to 5 percent by weight of a representative mineral topsoil. The major components of SOM are carbon (52 to 58 percent), oxygen (34 to 39 percent), hydrogen (3.3 to 48 percent), and nitrogen (3.7 to 4.1 percent). SOM is the major soil source of phosphorus and sulfur and basically the only source of nitrogen. Additionally, SOM is the major source of energy for soil microorganisms (ref A1 and A3).

SOM significantly affects soil properties. SOM acts as a granulator of the mineral particles and results in loose soil conditions. SOM affects soil structure, water-holding capacity, aeration, and aggregation. SOM has a high propensity to absorb cations. This phenomenon is known as cation exchange capacity (CEC). SOM is a sorbent of plant macronutrients and micronutrients, heavy metal cations, and organic materials such as pesticides because of its high specific surface and CEC (ref A3).

The liquid phase of soil (soil water) is an important soil property. Soil water is held within soil pores and makes up the soil solution. The physical properties of most fine-grained soils are controlled by the content of water. If clay has a proportionally large amount of water, the clay may appear plastic; however, if more water is added the clay may approach a liquid state.

The gas phase of soil (soil air) differs from the atmosphere in that soil air is not continuous, but is located in soil pores. Soil also has higher moisture content than the atmosphere. In addition, the carbon dioxide content of soil air is often several hundred times greater than the 0.03 percent typically found in the atmosphere (ref A1 and A4).

In contrast to the soil water and air fractions, soil solids contain many different minerals, some crystalline and some amorphous. When a soil solution becomes supersaturated with a mineral, the mineral can precipitate from solution. This can continue until the soil reaches equilibrium. If a soil solution is undersaturated, the undersaturated mineral can dissolve until a new equilibrium is reached. The factors that affect the mineral content of a soil solution are given in Table A-2; however, the composition of the soil is primarily controlled by the mineral phases of the soil. The accessibility of soil elements to plant uptake is influenced by the concentration of the element in soil solution and the ability of solids in soils to replenish elements that are depleted from solution (ref A2).

TABLE A-2. FACTORS THAT AFFECT SOIL SOLUTIONS

Factors
Air
Nutrient uptake by plants
Exchangeable ions and surface adsorption
Organic matter and microorganisms
Solid phases and minerals
Rainfall, evaporation, and drainage
Addition of fertilizer

Source: Xintaras, 1992, Agency for Toxic Substances and Disease Registry (ATSDR), 2001.

The elements that are found in the highest quantities in the Earth's crust are oxygen, silicon, aluminum, iron, carbon, calcium, potassium, sodium, and magnesium (Table A-3). A trace element is an element that is present at a level less than 0.1 percent in natural materials. Trace metals, heavy metals, and trace inorganic elements are considered trace elements.

TABLE A-3. ELEMENTS IN SOILS, EARTH'S CRUST, AND SEDIMENT

Element	Symbol	Soils, mg kg^{-1}		Earth's Crust, mg kg^{-1}	Sediments, mg kg^{-1}
		Median	Range	Mean	Mean
Aluminum	Al	72,000	700- <10,000	82,000	72,000
Arsenic	As	7.2	<0.1-97	1.5	7.7
Boron	B	33	<20-300	10	100
Barium	Ba	580	10-5,000	500	460
Beryllium	Be	0.92	<1-15	2.6	2
Bromine	Br	0.85	<0.5-11	0.37	19
Carbon (total)	C	25,000	600-370,000	480	29,400
Calcium	Ca	24,000	100-320,000	41,000	66,000
Cadmium	Cd	__	__	0.11	0.17
Chlorine	Cl	__	__	130	190
Cobalt	Co	9.1	<3-70	20	14
Chromium	Cr	54	1-2,000	100	72
Cesium	Cs	__	__	3	4.2
Copper	Cu	25	<1-700	50	33
Fluorine	F	430	<10-3,700	950	640
Iron	Fe	26,000	100->100,000	41,000	41,000
Gallium	Ga	17	<5-70	18	18
Germanium	Ge	1.2	<0.1-2.5	1.8	1.7
Mercury	Hg	0.09	<0.01-4.6	0.05	0.19
Iodine	I	1.2	<0.5-9.6	0.14	16
Potassium	K	15,000	50-63,000	21,000	20,000
Lanthanum	La	37	<30-200	32	41
Lithium	Li	24	<5-140	20	56
Magnesium	Mg	9,000	50->100,000	23,000	14,000
Manganese	Mn	550	<2-7,0000	950	770
Molybdenum	Mo	0.97	<3-15	1.5	2
Nitrogen	N	__	__	25	470
Sodium	Na	12,000	<500-100,000	23,000	5,700
Niobium	Nb	11	<10-100	20	13
Neodymium	Nd	46	<70-300	38	32
Nickel	Ni	19	<5-700	80	52
Oxygen	O	__	__	474,000	486,000
Phosphorus	P	430	<20-6,800	1,000	670
Lead	Pb	19	<10-700	14	19
Rubidium	Rb	67	<20-210	90	135
Sulfur (total)	S	1,600	<800-48,000	260	2,200
Antimony	Sb	0.66	<1-8.8	0.2	1.2
Scandium	Sc	8.9	<5-50	16	10
Selenium	Se	0.39	<0.1-4.3	0.05	0.42
Silicon	Si	310,000	16,000-450,000	277,000	245,000

TABLE A-3 (CONT'D)

Element	Symbol	Soils, mg kg^{-1}		Earth's Crust, mg kg^{-1}	Sediments, mg kg^{-1}
		Median	Range	Mean	Mean
Tin	Sn	1.3	<0.1-10	2.2	4.6
Strontium	Sr	240	<5-3,000	370	320
Thorium	Th	9.4	2.2-31	12	9.6
Titanium	Ti	2,900	70-20,000	5,600	3,800
Uranium	U	2.7	0.29-11	2.4	3.1
Vanadium	V	80	<7-500	160	105
Yttrium	Y	25	<10-200	30	40
Ytterbium	Yb	3.1	<1-50	3.3	3.6
Zinc	Zn	60	<5-2,900	75	95
Zirconium	Zr	230	<20-2,000	190	150

Source: Sparks, 1995.

A.2 Lead

In this study, lead (Pb) is the major contaminant (or trace element) of concern due to its concentration and toxicity. Lead is a heavy metal with a density of 11.4 g/cc. It is bluish-gray in color with an atomic number of 82 and a weight of 207.19 atomic mass units. Lead is soft and very malleable, is lustrous when freshly cut, tarnishes when exposed to air, and is a solid at 25 ^{o}C (ref A5). Lead was one of the first metals to be recognized, used by humans, and extracted from its ore. The first lead mines were discovered in Greece before 3000 BC, and lead was used in art, medicine, and technology by these ancient civilizations (ref A6). Because of the ease of working with lead and the fact that it is slow to corrode, lead was the second most used metal (after iron) in early history. The use of lead continued to be significant until the beginning of the 20th Century (ref A7). Because of the widespread nature of lead ores, cerussite ($PbCO_3$) and gelena (the sulfide PbS), and the ease of extraction, more than 300 million metric tons of lead have been produced throughout history. Lead is considered to be the most abundant metallic element that has ever been used by industry (ref A6 and A7).

Although lead has been beneficial to humans, it is now considered toxic and poses a threat to humans and animals. The major environmental sources for lead exposure are shown in Table A-4 (ref A8 and A9).

TABLE A-4. MAJOR ENVIRONMENTAL SOURCES OF LEAD EXPOSURE

Sources of Exposure
Ingestion of lead-based paints
Drinking water that has passed through lead pipes
Breathing or ingesting contaminated soil, dust, air, or water near waste sites that have elevated lead levels
Eating foods grown on soil that contains lead
Exposure to gasoline that contains lead
Occupational exposure such as recycling, battery manufacturing, and firing ranges

Source: Xintaras, 1992, ATSDR, 2001.

A.2.1 Lead in Soil

Lead is a natural component of the Earth's crust. The amount of lead found naturally depends on the mineral type. Plutonic rock and bauxites have reported lead concentrations averaging 16 mg/kg and 145 mg/kg, respectively. Over time the lead concentration of surface soils has increased as a result of industrial activities. Unimpacted soils from preindustrial periods have lead concentrations ranging from 0.1 to 1 mg/kg of soil, but today the average lead content of surface soil is 30 mg/kg (ref A10).

Typically lead found in surface soil is in the form of an ionic lead that has been adsorbed onto the clays, hydroxides, or organic fractions of the soil. Lead is also found in the soils in the form of lead oxide, sulfide, or other ionic salts. The majority of lead in ores is in the form of galena (lead sulfide, PbS), anglesite (lead sulphate, $PbSO_4$), minim (lead oxide, Pb_3O_4), and cerussite (lead carbonate, $PbCO_3$) (ref A11).

Lead is typically found naturally in soil or geologic materials combined with more than 200 minerals (ref A12). The form of lead will control the solubility and bioavailability of lead in soils. The sorption of lead onto soil is dependent on the pH of the soil (ref A10). The predominant forms of lead in soils with a pH <7.0 are the lead cation Pb^{2+}, lead sulfate ($PbSO_4$), and lead associated with organic material. In alkaline soils, the major forms of lead are lead carbonate ($PbCO_3$), lead hydroxide ($PbOH^+$), and lead associated with the organic material of soil.

The pH of the soil will affect the solubility of the lead compound. Thus, alkaline soils may contain forms of lead that will be more readily soluble (such as $PbCO_3$ and $PbOH^+$), while acidic, reducing soils will contain less soluble and less bioavailable forms of lead ($PbSO_4$ and PbS) (ref A12). The dissolution and migration of lead in soils depends upon the following factors:

- The solubility of the original lead solids.

- The formation and solubility of secondary lead products produced by alteration or weathering.

- The geochemistry of the soil matrix: the water content, pH, percent clay, amorphous ferric and manganese hydroxides, and permeability of the soil (ref A13).

Phosphates, carbonates, and sulfides are very active in controlling the solubility of lead because less soluble lead compounds are formed (ref A14).

A.2.2 Small Arms Firing Ranges

Typically, small arms firing ranges contain a firing line and impact berm. This berm is used as a backstop for trapping bullets fired during military training exercises. There are several types of small arms firing ranges, including recreational small arms firing ranges, such as skeet shooting ranges, and government small arms firing ranges, used primarily by the military. Small arms firing ranges can be indoor or outdoor.

A.2.3 Lead at Small Arms Firing Ranges

Lead is spread over the land in low concentrations when ammunition is used for hunting. In contrast, lead in soils at firing ranges is concentrated and can be a significant source of lead pollution in the environment. Corrosion of spent ammunition occurs as a result of weathering of lead bullets. As the water evaporates, the lead ions will adsorb to the soil. As a result, lead contaminated soils are found at small arms firing ranges that have been in operation for many years. Lead has been found at 10 to 100 times greater amounts in soil at firing ranges than in the soil of the surrounding countryside. Typically when elevated lead is measured at the surface, the subsurface also contains elevated lead. This is an indication that there is mobilization of lead through the soil profile. Additionally, the small arms firing range lead concentrations in the surface water and in plants are higher than those grown in uncontaminated soil (ref A14).

The berms at small arms firing ranges contain spent bullets, shattered fragments, small particles, and lead smears on larger sand grains as a result of many years of use. The larger particles can be removed by screening the soil; however, the smaller particles and grains of ammunition remain and corrode with time and weathering. These smaller particles are a major environmental problem. The smaller particles move through the soil and into groundwater. They may also migrate off the small arms firing range and into nearby lakes and streams (ref A15).

The primary reason for lead mobilization in soils is lead dissolution and oxidation to form lead carbonates or lead sulfate compounds. When lead bullets come in contact with the soil, the lead may be subject to oxidation, carbonation, and hydration. These reactions dissolve elemental lead and the lead enters the environment at a weathering rate of 1 percent per year. The rate of lead oxidation and the products from weathering of lead are variable according to the geographical location; therefore, the threat of lead to the environment from firing ranges depends upon the soil conditions and location of the range. Because shooting ranges are known to contain major amounts of lead from ammunition, Craig et al studied the transport of lead from a heavily used shooting range in Virginia into the surrounding environment (ref A7). The authors

compared samples of surface waters taken from 16 sites near the shooting range with the lead concentrations of natural ground waters. The concentration of lead in the water from the shooting range varied from 0.5 to 473 ppb. The lowest levels were found in streams outside the shooting area.

Lead mobility and leachability are low in soils containing high amounts of iron and aluminum oxides. Clay soils with high organic matter or CEC also have low lead mobility. These compounds do not form chemical compounds with lead but provide a large surface area for lead adsorption. Researchers have estimated that all of the metallic lead pellets contained in Denmark soil will be transformed to soluble lead within 100 to 300 years (ref A14). At shooting ranges in Sweden, an average of 5 percent of metallic lead has been transformed to lead carbonate and lead sulfate in as little as a 20 to 25 year period. Typically, these transformed lead products are primarily composed of cerussite, hydrocerussite, and anglesite (ref A16).

A.2.4 Standards for Lead in Soil/Water

In uncontaminated soils, lead concentrations vary from 2 to 200 ppm (ref A2 and A17). In contrast and according to USEPA guidelines, soils with concentrations of lead above 300 mg/kg^{-1} are considered contaminated. When concentrations exceed 400 mg/kg^{-1}, remediation is required (ref A17).

In "Interim Guidance on Establishing Soil Lead Cleanup Levels at Superfund Sites," (ref A49) the U.S. Environmental Protection Agency (USEPA) Office of Solid Waste and Emergency Response (OSWER) established a guideline for total lead in soil in September 1989. OSWER recommended that total lead levels in soil be between 500 and 1000 mg/kg soil (ref A18). Since this level was offered as a guideline and not a standard, many states have set their own standards for total lead concentrations in soil.

Regulation of lead in soil is also based on leaching tests. A list of hazardous contaminants including lead is regulated with the Toxicity Characteristic Leachate Procedure (TCLP), USEPA method 1311 (ref A19). The TCLP is a leaching test that uses a weak acetic acid solution. This leaching test is used to classify waste as hazardous. A waste is considered hazardous if TCLP leach concentrations are >5 mg/L (ref A19).

A.3 Lead in the Human Body

Lead is not a critical element to sustain life; in fact, lead serves no purpose in the human body. Inorganic lead in the body is absorbed and then distributed into the blood; soft tissue such as kidney, bone marrow, liver and brain; and tissues that contain larger amounts of minerals such as bones and teeth. Tissues that have a high mineral content such as bone contain 95 percent of the lead found in the adult body. In blood, 99 percent of the lead is found with the red blood cells or erythrocytes. When lead is absorbed in the body, lead has a half-life of 25 days in the blood, 40 days in soft tissues, and more than 25 years in the bone (ref A8). An ATSDR (ref A20) report stated that there is a highly significant correlation between higher than normal lead levels in children and exposure to lead in dust and soil at levels of 500 to 1000 ppm (ref A8 and A21). There is a strong correlation between lead exposure and lead levels in the blood. The levels increase 3 to 7 µg/dl for every 1000-ppm increase of lead in the soil or dust

(ref A8). Inorganic compounds containing lead are transformed into lead phosphate complexes in the body. The lead phosphate most likely to be formed in the human body is in the form of hydroxypyromorphite. The following equation represents the precipitation of hydroxypyromorphite in the body.

$$5Pb^{2+} + 3HPO_4^{2-} + H_2O \rightarrow Pb_5(PO_4)_3OH + 4H^+ \qquad [A1]$$

A.4 Health Effects of Lead

The harmful effect of lead on humans was reported as early as the 16th Century (ref A7). Hippocrates and Nikander, two early physicians, were the first to recognize symptoms of anemia, colic, neuropathy, sterility, and coma in workers as a result of an exposure to lead more than 2000 years ago (ref A6). Lead poisoning is a chronic problem. Lead exposure can result in damage to the peripheral nervous system and affect memory, vision, and muscle coordination, causing weakness in the fingers, wrists, and ankles. High levels of lead in the body can damage kidneys, cause anemia, miscarriage, and decreased fertility. Some forms of lead have been noted to be carcinogens in animals (ref A21). Additional adverse health effects related to exposure to lead include impaired mental and physical development, decreased hemoglobin biosynthesis, impaired hearing, and decreased levels of vitamin D in the blood. Some studies have shown that neurobehavioral effects like poor academic performance, lowered intelligence (measured by intelligence quotient (IQ) tests), learning disabilities, hearing loss, reduced attention span, behavioral abnormalities, and deficits in motor skills may continue even after lead levels in the blood are returned to normal (ref A8 and A22). The established adverse effects of lead on human health are given in Table A-5.

The absorption of lead through the human gastrointestinal tract varies with age, diet, and nutritional status. In addition, the chemical form and particle size of the lead have a large effect on absorption (ref A23). Lead in water is more efficiently absorbed than lead ingested in food (ref A24).

Children and fetuses are the most likely groups to have serious ill effects from lead due to their developing nervous systems. This increased susceptibility to the neurotoxic effects of lead is because lead absorption through the gastrointestinal tract is more efficient and thus greater in children (ref A8). Adults usually absorb 7 to 15 percent of lead while children absorb 40 to 53 percent of lead through diet (ref A23). Lead exposure to children is a major concern.

Rabinowitz predicted the theoretical distribution of blood lead in two groups of children hypothetically exposed to lead contaminated soil (ref A11). One group was exposed to soil treated with phosphate to reduce the lead bioavailability. The other group was exposed to untreated soil. The untreated soil contained 1337 μg/g of available lead while the treated soil contained 764 μg/g of available lead. The untreated soils produced a blood-level distribution of 8.5 μg/dl (with 32 percent of the children having more than 10 μg/dl and 5.2 percent having more than 15 μg/dl). The treated soils produced a blood level of 5.4 μg/dl (with only 4 percent of the children having more than 10 μg/dl and 0.2 percent having more than 15 μg/dl). Based on these results, the soil treatment was believed to have reduced the bioavailable lead.

TABLE A-5. ESTABLISHED ADVERSE EFFECTS OF LEAD ON HUMAN HEALTH

System	Effect
Cardiovascular	Increased blood pressure. Left ventricular hypertrophy. Electrocardiographic abnormalities.
Endocrine/metabolic	Decreased thyroxine levels in adults. Decreased 1,25-dihydroxy vitamin D in children's serum.
Gastrointestinal	Colic
Hematologic	Increased ALA synthetase activity. Decreased ALA dehydratase activity. Increased ALA in blood, plasma or urine. Increased erythrocyte protoporphyrin. Increased zinc protoporphyrin in children. Increased urine coproporphyrin. Decreased hemoglobin. Decreased pyrimidine-5in.-nucleotidase activity in children.
Immune	Decreased cell-mediated immune function
Nervous	Encephalopathy . Neurological symptoms and signs Impaired peripheral nerve conduction. Reduced neurobehavioral test performance. Reduced auditory acuity in children.
Renal	Chronic nephropathy. Renal impairment with gout or hypertension. Aminoaciduria-Fanconi Syndrome in children.
Reproductive	Increased frequency of stillbirth. Increased frequency of spontaneous abortion. Reduced sperm production or motility. Increased percent abnormal spermatocytes.
Developmental	Reduced growth in children. Impaired mental development in children. Decreased birth weight or head circumference. Decreased gestational age at birth. Increased neonatal death ratio.

Source: Jin et al, 1997.

ALA = Delta-Aminolevulinic Acid

A.5 Standards for Lead in Humans

Exposure to lead can cause lead-induced cognitive dysfunction that occurs when lead in the blood and brain reach levels that result in neurological behavioral changes (ref 25). The Center for Disease Control (CDC) has estimated that one in every eleven children in the U.S. under the age of 6 has elevated levels of lead in their blood. Toxicity is observed when lead blood levels reach 10 to 15 µg/dl. More than one million children living in the U.S. have lead

blood concentrations at this amount or higher (ref A8, A22, and A24). A blood lead level of 40 μg/dl has been shown to produce clinical anemia in children. Decreases in IQ, hearing, and growth in children have been observed when blood lead levels reach 30 μg/dl (ref A18). Intelligence levels of children are affected when lead levels are above 10-20 μg/dl (ref A22). Table A-6 presents an interpretation of follow-up activities recommended for children with varying blood lead concentrations (ref A8).

TABLE A-6. INTERPRETATION OF BLOOD LEAD TEST RESULTS AND FOLLOW-UP ACTIVITIES: CLASS OF CHILD BASED ON BLOOD LEAD CONCENTRATIONS

Class	Blood lead concentration, μg/dl	Comment
I	< 9	A child in Class I is not considered to be lead poisoned.
IIA	10-14	Many children (or a large proportion of children) with blood lead levels in this range should trigger community-wide childhood lead poisoning prevention activities. Children in this range need to be screened more frequently.
IIB	15-19	A child in Class IIB should receive nutritional and educational interventions and more frequent screening. If the blood lead levels persist in this range, environmental investigation and intervention should be done.
III	20-44	A child in Class III should receive environmental evaluation and remediation and a medical evaluation. Such a child may need pharmacologic treatment of lead poisoning.
IV	45-69	A child in Class IV will need both medical and environmental interventions, including chelation therapy.
V	> 70	A child in Class V lead poisoning is a medical emergency. Medical and environmental management must begin immediately.

Source: Xintaras, 1992.

Prior to 1991, the CDC set 30 μg/dl as the maximum safe blood lead level for an individual child and 15 μg/dl as the average for a population; however, this level for children is considered to be high. In 1991, the CDC set the current standard for lead as10 μg/dl of blood (ref A21).

Although adults may have a higher level of blood lead before symptoms appear, the CDC and ATSDR state that blood levels of 10-15 μg/dl can produce lead toxicity (ref A18). The 1988 ATSDR report estimated that 2.4 million children from the age of 6 months to 5 years had blood lead levels above 15 μg/dl (ref A20). In addition, 200,000 children have been identified in the U.S. with blood lead levels above 25 μg/dl (ref A8).

A.6 Bioavailability of Lead

Bioavailability is a term which generally refers to the ability of a chemical to accumulate in living systems. Typically bioavailability tests are used to determine the ability of the human gastrointestinal tract to absorb lead (ref A25). The USEPA deems the absolute bioavailability of lead in the food and water is 50 percent and the absolute bioavailability of lead in soil is 30 percent for children (ref A23). Simple in vitro tests have been designed to simulate the human gastrointestinal tract to evaluate bioavailability of metals, particularly iron from food. These tests have been adapted for use to measure and determine the bioavailability absorption of lead and have been compared to the results of swine and rat model tests. The Solubility-Bioavailability Research Consortium (SBRC) was formed to further the development and acceptance of these methods for estimating the bioavailability of metals from contaminated soils. The SBRC developed an extraction test that has produced results that correlate with the swine model studies of lead bioavailability (ref A12 and A23). Ruby et al (ref A26 and A27) developed and are currently validating what is termed the Physiologically Based Extraction Test (PBET) for estimating the lead in soil. This is based on the fact that the bioavailability in an animal model (or in humans) will be controlled by the form and solubility of lead in the soil. Although validation trials are not yet complete, the PBET appears to produce consistent results at a wide pH range and is sensitive to many different types of materials that contain lead. The PBET potentially offers a quick and cost effective method to estimate bioavailability.

The primary concern in treating soils that contain lead is to reduce the bioavailability of the lead to acceptable levels for human safety (ref A28 and A29). The chemical and physical form of lead in the soil has a major impact on its bioavailability. Studies in rats and swine have shown that the absorption of lead from soil will vary from near 0 to more than 50 percent absolute bioavailability depending on the source of lead (ref A12). Lead animal feeding studies have shown that the oral bioavailability of lead sulfide and lead chromate is less than that of lead oxide and lead acetate (ref A8). Also, an increased particulate size can reduce the bioavailability of lead in the gastrointestinal tract. Studies show decreasing the size from 197 microns to 6 microns results in increasing the absorption of lead by 500 percent (ref A8). Nutritional deficiencies of essential metals, specifically calcium, iron, and zinc, increase the hazard of lead. This is believed to result in the increase of the absorption and toxicity of dietary lead (ref A24).

Changing the form of lead in the soil to a less soluble form can be an excellent alternative for remediation of lead contaminated soil (ref A13). Treating the soil with lime, peat, or chelators modifies the uptake of lead by plants; however, these treatments may not reduce the bioavailability of lead in the human stomach due to the pH level of gastric secretions. For example, lead sulfide is normally an insoluble lead compound, but when ingested by humans, lead sulfide is absorbed at rates similar to lead nitrate (ref A11 and A30).

There is a relationship between the solubility and bioavailability of a substance. The solubility of lead in the soil can be used as an indicator to approximate the bioavailability of the lead (ref A17). Generally metals that have a greater solubility have a high dissolution rate and therefore are more bioavailable. The solubility of a metal (M) will be different depending on the compound containing the metal. The solubility of metal contaminants can be reduced by changing the form of the metal, for example from a metal carbonate to a metal phosphate, to

significantly lower the solubility. Therefore, *in situ* reduction of the solubility of a contaminant rather than the complete removal can be an important remediation alternative (ref A31). The general dissolution reaction for a metal complex M_xL_y follows:

$$M_xL_y\ (s) \Leftrightarrow xM^{y+}\ (aq) + yL^{x-}\ (aq) \qquad [A2]$$

Where: xM^{y+} (aq) and yL^{x-}(aq) are aqueous metal and ligand ions of M and L, respectively.

The equilibrium constant for the reactions is:

$$K \equiv \frac{[M^{y+}]^x\ [L^{x-}]^y}{[M_xL_y]} \qquad [A3]$$

Where: [ ] denotes activities.

The solubility product is defined as:

$$K_{sp} = K[M_xL_y] \qquad [A4]$$

If the solid M_xL_y is in the standard state then its activity is unity and K equals $K_{sp.}$ If L^{x-} has a fixed activity, a solid with the smallest value for K_{sp} will provide the smallest equilibrium activity of M^{y+}. According to the solubility product of equation [A4], the most soluble form of the solid will be the metal that has the largest aqueous equilibrium activity of M^{y+} (ref A31).

Although most research on lead bioavailability has concentrated on the solubility of the mineral, Davis et al (ref A32) looked at the relative mass contribution of near-surface and surface-bound lead as related to bioaccessibility. He reports that the total mass of lead that dissolves in the stomach is not absorbed into the body. Solubilized lead may not be absorbed because of precipitation and sorption reactions in the small intestine. The following formula represents Davis' mass balance of lead in soil:

$$\Sigma Pb\ (\text{analytical total}) = \text{mineral Pb mass} + \text{surface Pb mass} \qquad [A5]$$

A.7 Solubility of Lead Phosphates

Nriagu (ref A33 and A34) measured the solubility products for the pyromorphite minerals ($Pb_5(PO_4)_3OX$) with X being in the form of halide or hydroxide chloro- ($10^{-84.4}$) bromo- ($10^{-78.1}$), hydroxy- ($10^{-76.8}$), and fluoropyromorphite ($10^{-71.6}$). Nriagu's work indicated a thermodynamic stability sequence for lead pyromorphites of $Pb_5(PO_4)_3Cl > Pb_5(PO_4)_3Br > Pb_5(PO_4)_3OH > Pb_5(PO_4)_3F$. Based on Nriagu's research, other researchers investigated the solubility of lead compounds and a comparison of the solubililty products of selected lead minerals is given in Table A-7 (ref A13 and A31). As presented in this table, lower values of K_{sp} represent insoluble compounds.

TABLE A-7. SOLUBILITY PRODUCTS OF SELECTED LEAD MINERALS

Lead Phase	Chemical Composition	Log K_{sp}
Litharge	PbO	12.9
Anglesite	$PbSO_4$	-7.7
Cerussite	$PbCO_3$	-12.8
Galena	PbS	-27.5
Chloropyromorphite	$Pb_5(PO_4)_3Cl$	-84.4
Hydroxypyromorphite	$Pb_5(PO_4)_3OH$	-76.8
Fluoropyromorphite	$Pb_5(PO_4)_3F$	-71.6
Bromopyromorphite	$Pb_5(PO_4)_3Br$	-78.1
Corkite	$PbFe_3(PO_4)(SO_4)(OH)_6$	-112.6
Hinsdalite	$PbAl_3(PO_4)_2(SO_4)(OH)_6$	-99.1
Plumbogummite	$PbAl_3(PO_4)_2(OH)_5 \cdot H_2O$	-99.3

Source: Ruby et al, 1994, Traina & Laperche, 1999.

K_{sp} = solubility constant product

Nriagu (ref A35) showed that hydroxypyromorphite is produced from the alkaline hydrolysis of secondary lead orthophosphate. The ionization of secondary lead orthophosphate derived by Nriagu (ref A36) follows.

$$PbHPO_4 \rightarrow Pb^{2+} + HPO_4^{2-} \qquad [A6]$$

$$Ksp[PbHPO_4] = \frac{k_2 \,.\, a_{Pb}^{2+} \,.\, a_{H2PO4}}{a_{H+}} \qquad [A7]$$

If sufficient phosphate is present, pyromorphite will form in soils contaminated with lead. In pyromorphite, the mass ratio of lead to chlorine is 23.3 to 1, which suggests that very small quantities of phosphorus and chlorine in relation to lead are necessary for halide pyromorphite to form (ref A37).

Phosphate can produce highly insoluble lead phosphates, such as the pyromorphite, as shown in equation [A8], and thus reduce the bioavailability of the lead to humans.

$$10M^{2+} + 6H_2PO_4^- + 2OH^- \rightarrow \underline{M_{10}(PO_4)_6(OH)_2} + 12H+ \qquad [A8]$$

The rate of precipitation of pyromorphite is controlled by the availability of soluble lead and phosphorus; the reaction is shown in the following equation (ref A38).

$$5Pb^{2+} + 3H_2PO_4^- + Cl^- \leftrightarrow \underline{Pb_5(PO_4)_3Cl_{(s)}} + 6H^+$$

$$\log K = -25.05 \qquad [A9]$$

If the average lead content of soils is much less than that of phosphorus, phosphate may control the solubility of lead in soil (ref A2). The reaction of dissolved Pb^{2+} with hydroxyapatite can be described with sequential dissolution and precipitation reactions (ref A31):

$$Ca_5(PO_4)_3OH + 7H^+ \Leftrightarrow 5Ca^{2+} + 3H_2PO_4^- + H_2O \quad [A10]$$

$$5Pb^{2+} + 3H_2PO_4^- + H_2O \Leftrightarrow \underline{Pb_5(PO_4)_3OH} + 7H^+ \quad [A11]$$

Where ($\underline{Pb_5(PO_4)_3OH}$) is the mineral hydroxypyromorphite.

Combining these reactions provides the overall reaction as shown in equation [A12]:

$$Ca_5(PO_4)OH + 5Pb^{2+} \Leftrightarrow \underline{Pb_5(PO_4)_3OH} + 5Ca^{2+} \quad [A12]$$

Pyromorphite is much less soluble than most lead minerals and is stable both chemically and biologically in the environment (ref A38). Zhang and Ryan (ref A39) demonstrated that the formation of chloropyromorphite from cerrusite and apatite is favored at gastrointestinal (GI) tract pH conditions. The conversion kinetics of soil lead to chloropyromorphite in the presence of apatite occurs quickly. Thus if lead and phosphate are available at the correct ratios when a human ingests soil-containing lead, the formation of chloropyromorphite may occur and this results in a low bioavailability of the lead.

A.8 Phosphorus/Phosphate in Soil

The phosphorus content of soils ranges from 200 to 5000 ppm, with an average of 600 ppm. Phosphorus is typically found in soils in the oxidation state +5. The stable form of phosphorus in soils is orthophosphate. Lead phosphates are present naturally in some soils. Nriagu (ref A34 and A36) stated that pyromorphite or chloropyromorphite, $Pb_5(PO_4)_3Cl$, and plumbogummite, $PbAl_3(PO_4)_2(OH)\cdot 5H2O$, are the most thermodynamically stable lead minerals found under normal conditions in the environment.

A.9 Phosphates for Treatment of Lead-Contaminated Soils

Phosphates have been known to stabilize lead for many years. To capitalize on the low solubility of lead phosphate complexes, phosphates have been added to lead contaminated soil to produce insoluble lead. When there is sufficient phosphorus available, lead-phosphates will form at the expense of other lead-containing compounds (ref A12 and A31). Ruby et al (ref A13) suggested the use of phosphates to reduce the leaching, migration and bioavailability of lead. Recent studies have shown that the in situ phosphate treatment of metal-contaminated soil with phosphate binders can reduce lead levels below the RCRA standards for hazardous wastes. While phosphate binders can be used to form pyromorphites, the reaction kinetics have been shown to depend on the compound of phosphate (ref A40).

Researchers showed that finely ground phosphate rock added to lead contaminated soils reduces water-soluble lead by 57 to 100 percent. The process leaves the lead in the soil but renders it insoluble. Ma and Rao (ref A28) report that this form of lead cannot be absorbed after ingestion, and thus, cannot enter the bloodstream.

Traditionally, lead contaminated soil treatment technologies using phosphate have generally relied on triple super phosphate (TSP), phosphoric acid, or some form of a water soluble phosphate. These types of phosphate provide a high concentration of dissolved phosphate to the soil (ref A41). Hettiarachichi et al (ref A42) examined seven different phosphate treatments for lead contaminated soil as shown in Table A-8. They found a significant reduction in bioavailable lead when treated with phosphates. Increasing the amount of phosphorus from 2500 to 5000 mg/kg produced a significantly greater reduction in bioavailable lead. The effectiveness of phosphate rock in reducing the bioavailability of lead was equal to or greater than TSP or phosphate rock in 80 percent of the soils, when subjected to the PBET. The reductions in bioavailability of lead measured by PBET were apparent 3 days after treatment; however, no additional reductions in lead bioavailability were observed for up to 365 days after treatment.

TABLE A-8. PHOSPHATE TREATMENTS EXAMINED BY HETTIARACHICHI

Treatment
Unamended control
2500 mg P/kg as TSP
Phosphate rock
Acetic acid followed by TSP
Acetic acid followed by phosphoric acid
5000 mg P/kg soil TSP followed by 5000 mg P/kg as phosphate rock

Source: Hettiarachichi, 2001.

TSP = Triple super phosphate.

Apatite ($Ca_{10}(PO_4)_6(OH,F,Cl)_2$) is a mineral containing phosphate. Apatite minerals form naturally and are considered to be stable over billions of years. The apatite mineral group consists of hexagonal crystals and has three dominant members OH in hydroxyapatite, fluoride in fluorapatite, and chlorine in chlorapatite (ref A31). Bone ash and bone char have the same molecular formula as hydroxyapatite and have been used by industry for lead remediation. The structure of apatite is stable in many extreme conditions maintaining a pH between 2 and 12 in up to 1000 ^{o}C, with aqueous and nonaqueous phase liquids (ref A30).

Apatites have been examined for their ability to remove toxic metal ions from wastewater and aquatic solutions. Lead remediation with apatite produces minerals that are durable and leach resistant. As little as 1 percent of apatite by weight can adequately treat most soils that contain metals (ref A40). In 1993, Ma et al (ref A43) conducted a study to develop a technology for immobilizing lead in situ with apatite. They reported that soluble phosphorus is the major factor for lead immobilization by apatite. Since the solubility of apatite is controlled by the pH, the pH is a crucial parameter in the immobilization process. Ma et al (ref A43) suggested that dissolved lead is removed from solution through hydroxyapatite dissolution and pryomorphite precipitation and that the dissolution-precipitation process is the primary mechanism for lead immobilization.

There are three types of reactions that may control lead immobilization by hydroxyapatite: surface adsorption, cation substitution, and precipitation. Lead bonds with the apatite mineral structure during precipitation of new solids, such as lead-apatite, or by exchanging with calcium in an existing calcium-apatite (ref A31). Hydroxyapatite has the ability to convert soil-bound lead, lead carbonate, or lead sulfide to pyromorphite. This reaction will occur rapidly at a pH less than 4; however, at a higher pH, the conversion is slower. The solubility of hydroxyapatite and chloropyromorphite at various pH values is given in Table A-9 (ref A44).

TABLE A-9. SOLUBILITY OF PHOSPHATE COMPOUNDS AT VARIOUS PH VALUES

pH	Solubility of hydroxyapatite $Ca_5(PO_4)_3OH$(mol/l)	Solubility of chloropyromorphite $Pb_5(PO_5)_3Cl$ (mol/l)
5	6.30×10^{-2}	1.58×10^{-8}
6	3.16×10^{-4}	3.98×10^{-10}
7	1.58×10^{-6}	1.99×10^{-10}
8	5.01×10^{-8}	1.58×10^{-11}

Source: Lindsay, 1979.

Manecki et al (ref A45) studied the effect of aqueous lead on the kinetics of the dissolution of apatite. Synthetic microcrystalline hydroxylapatite (HAP), natural chlorapatite (CAP), and fluorapatite (FAP) were used in batch experiments at pHs of 4.2 to 7.0 at 22 ^{o}C and in the presence of aqueous chlorine. These experiments were conducted with 1 gram of apatite per liter for the three forms of apatites. The dissolution rate constants were adjusted for particle specific surface area and the results showed that dissolution of CAP was greater than either FAP or HAP. All three phosphate forms had an initial rapid release of calcium and phosphorus during the first few hours of testing with a decrease in release rate thereafter. When aqueous lead and chlorine were present, all of the apatites formed pyromorphite. The rate of lead uptake by the apatites tracked the dissolution rate constants of apatite>HAP>CAP>FAP. This suggests that the total concentration of phosphate available in the system regulated the uptake of lead. Study results show that HAP and CAP stabilized more than 98 percent of the lead in two weeks, and FAP only stabilized 30 percent of the lead (ref A45). The kinetics of apatite dissolution in the absence and presence of lead for this study are shown in Tables A-10 and A-11, respectively (ref A45).

Seaman et al (ref A46) studied the immobilization of lead by adding hydroxyapatite to contaminated sediments from the Department of Energy's (DOE) Savannah River site. Application rates of 0, 5, 15.8, and 50 grams of hydroxyapatite per kg of soil were used. Evaluations using sequential extraction (a test that is used to determine the quantity and degree of solubility of metals) and TCLP indicated that hydroxyapatite transforms lead from exchangeable fractions to a less soluble form of lead.

Stanforth and Qui (ref A41) tested two samples of lead-contaminated soil, one from a rifle range and another from an industrial waste area, to determine the effect of phosphate treatment on the solubility of lead in soil. The soils were treated with different levels of sodium phosphate solutions at pH 7. Additionally, calcium di-hydrogen phosphate was used as a treatment additive for some samples. The phosphate treatment was added to the soil for 24 hours before testing. The treatments were evaluated at different reaction times and temperatures, and their effects on lead stabilization were studied. Phosphate addition to a lead contaminated soil reduced lead solubility in an acidic pH range but not in an alkaline range. Additionally, added chloride reduced lead solubility by about half, which was thought to be due to the formation of lead chloride (see Table A-12).

TABLE A-10. KINETICS OF APATITE DISSOLUTION IN THE ABSENCE OF LEAD

Parameter Measured	Kinetic equation (linear regression), $M\ hr^{-1}$	Correlation coefficient R^2	Apparent rate constant k_{Ap}, $mol\ g^{-1}\ hr^{-1}$	Dissolution constant k_{Ap}, $mol\ m^{-2}\ hr^{-1}$
HAP dissolution	$77.8 + 0.33_t$	0.983	3.3×10^{-8}	5.6×10^{-10}
(Ca)	$69.7 + 0.25_t$	0.985	4.2×10^{-8}	7.0×10^{-10}
(P)				
CAP dissolution	$58.4 + 0.13_t$	0.981	1.3×10^{-8}	4.3×10^{-9}
(Ca)	$35.7 + 0.065_t$	0.979	1.1×10^{-8}	3.7×10^{-9}
(P)				
FAP dissolution	$60.4 + 0.08_t$	0.995	0.8×10^{-8}	2.0×10^{-9}
(Ca)	$25.0 + 0.023_t$	0.981	0.4×10^{-8}	1.0×10^{-9}
(P)				

Source: Manecki, 2000.

TABLE A-11. KINETICS OF APATITE DISSOLUTION IN THE PRESENCE OF PB

Parameter Measured	Kinetic equation (linear regression) ($M\ hr^{-1}$)	Correlation coefficient R^2	Apparent rate constant k_{Ap} ($mol\ g^{-1}\ hr^{-1}$)	Dissolution constant k_{Ap} ($mol\ m^{-2}\ hr^{-1}$)
HAP dissolution (Ca)	$231.7 + 0.28_t$	0.963	2.8×10^{-8}	4.7×10^{-10}
CAP dissolution (Ca)	$93.4 + 0.35_t$	0.984	3.5×10^{-8}	1.2×10^{-8}
FAP dissolution (Ca)	$60.8 + 0.10_t$	0.961	1.0×10^{-8}	2.5×10^{-9}

Source: Manecki, 2000.

TABLE A-12. EFFECT OF DIFFERENT IONS ON THE SOLUBILITY OF LEAD PHOSPHATE UNDER ACIDIC CONDITIONS

Additive	pH	Lead concentration mg/L
TSP	2.70	97.6
TSP+NaF	2.96	61.8
TSP+NaCl	2.77	42.0
TSP+Na_2SO_4	2.76	78.8
TSP+$MgCl_2$	2.73	41.4
TSP+$CaCl_2$	2.67	38.8

Source: Stanforth and Qui, 2001.

TSP = Triple super phosphate.

Yang et al (ref A38) used phosphoric acid to reduce lead solubility and bioavailability in soil. Soil that contained 4360 mg of lead per kilogram was treated with H_3PO_4 to provide 1250, 2500, 5000, and 10,000 mg of lead per kilogram soil mass. Soluble lead concentration decreased as the H_3PO_4 increased. Approximately 23 percent of lead in the soil was redistributed from the clay and silt to the sand fractions of the soil. The treatment provided a compound similar to chloropyromorphite, although slightly more soluble, and the soil lead bioavailability was reduced.

Plant uptake studies have shown that plants grown in a lead-contaminated soil treated with natural and synthetic apatites have a decreased lead content in the shoot tissue. The lead content in the shoot tissue decreases as the quantity of added apatite is increased; however, the lead and phosphorus contents in the roots of the plants increase as the amount of added apatite is increased. The study indicates that the addition of apatite to contaminated soils can lower the bioavailability and increase the geochemical stability of lead in soil (ref A47).

Cao et al (ref A48) found a mixture of phosphoric acid and phosphate rock provided the best overall results for in situ lead immobilization with less change in soil pH and less leaching of phosphorus. The translocation of lead from the roots to the shoots in St. Augustine grass was significantly reduced with the phosphate treatments. This may be a result of the formation of chloropyromorphite on the cell walls of the roots. This study suggests that a combination of phosphoric acid with phosphate rock may be an effective remediation technology for lead-contaminated soils.

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A.11 Acronyms

ALA = Delta-Aminolevulinic Acid
ATSDR = Agency for Toxic Substances and Disease Registry
CAP = chlorapatite
CDC = Center for Disease Control
CEC = Cation Exchange Capacity
DOE = Department of Energy
FAP = fluorapatite
GI = gastorintestinal
HAP = hydroxylapatite
IQ = intelligence quotient
OWSER = Office of Solid Waste and Emergency Response
PBET = Physiologically Based Extraction Test
RCRA = Resource Conservation and Recovery Act
SBRC = Solubility-Bioavailability Research Consortium
SOM = soil organic matter
TCLP = Toxicity Characteristic Leachate Procedure
TSP = triple super phosphate
USEPA = U.S. Environmental Protection Agency

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APPENDIX B. METHOD DETECTION LIMITS

ICP PERKIN-ELMER DL-4300

Element	Method Detection Limits	
	Liquid, mg/L	Soil, mg/kg
Silver (Ag)	0.03	6
Arsenic (As)	0.02	4
Chromium (Cr)	0.03	6
Copper (Cu)	0.03	6
Nickel (Ni)	0.03	6
Lead (Pb)	0.02	4
Antimony (Sb)	0.02	4
Zinc (Zn)	0.03	6

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APPENDIX C. PARTICLE SIZE ANALYSIS CURVES

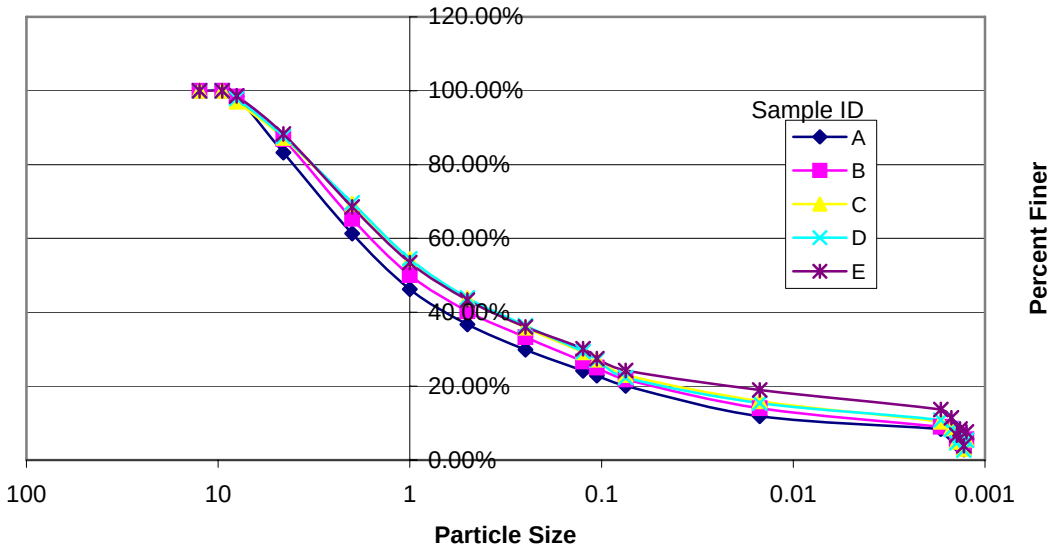

Figure C-1. Baseline particle size analysis for each sample.

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APPENDIX D. DIGESTION STUDY DATA BAR GRAPHS

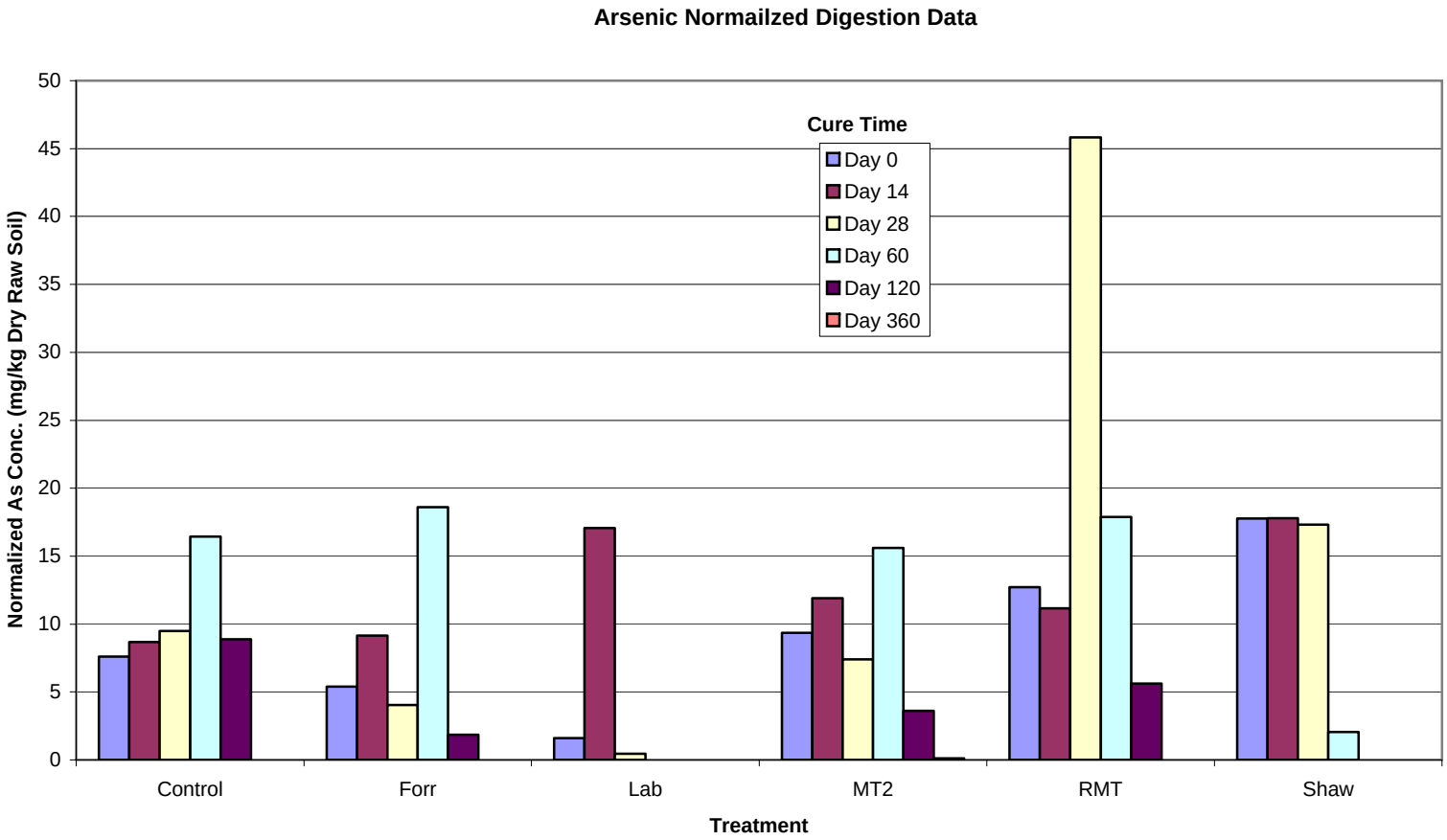

Figure D-1. Normalized digestion data for arsenic.

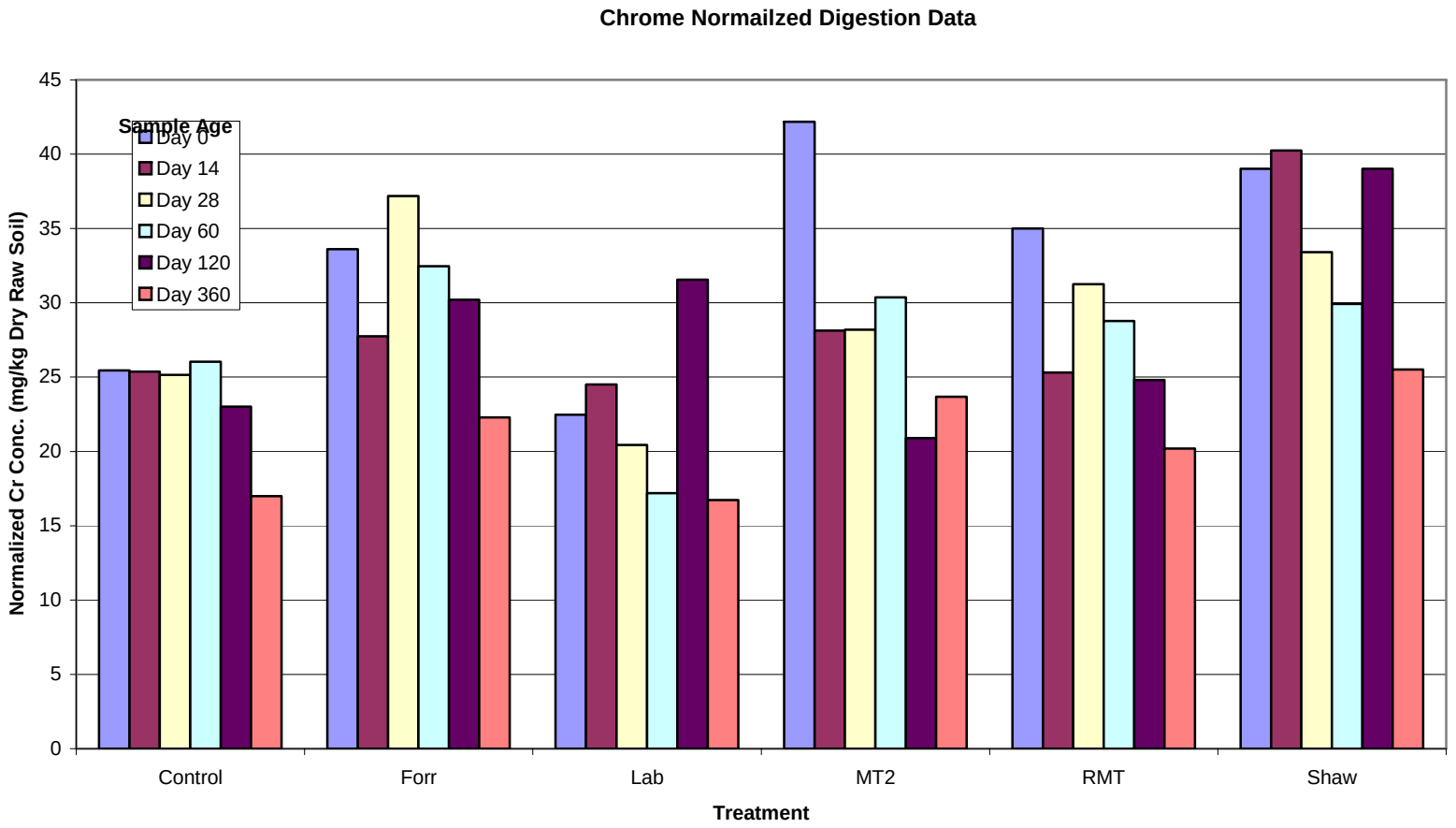

Figure D-2. Normalized digestion data for chromium.

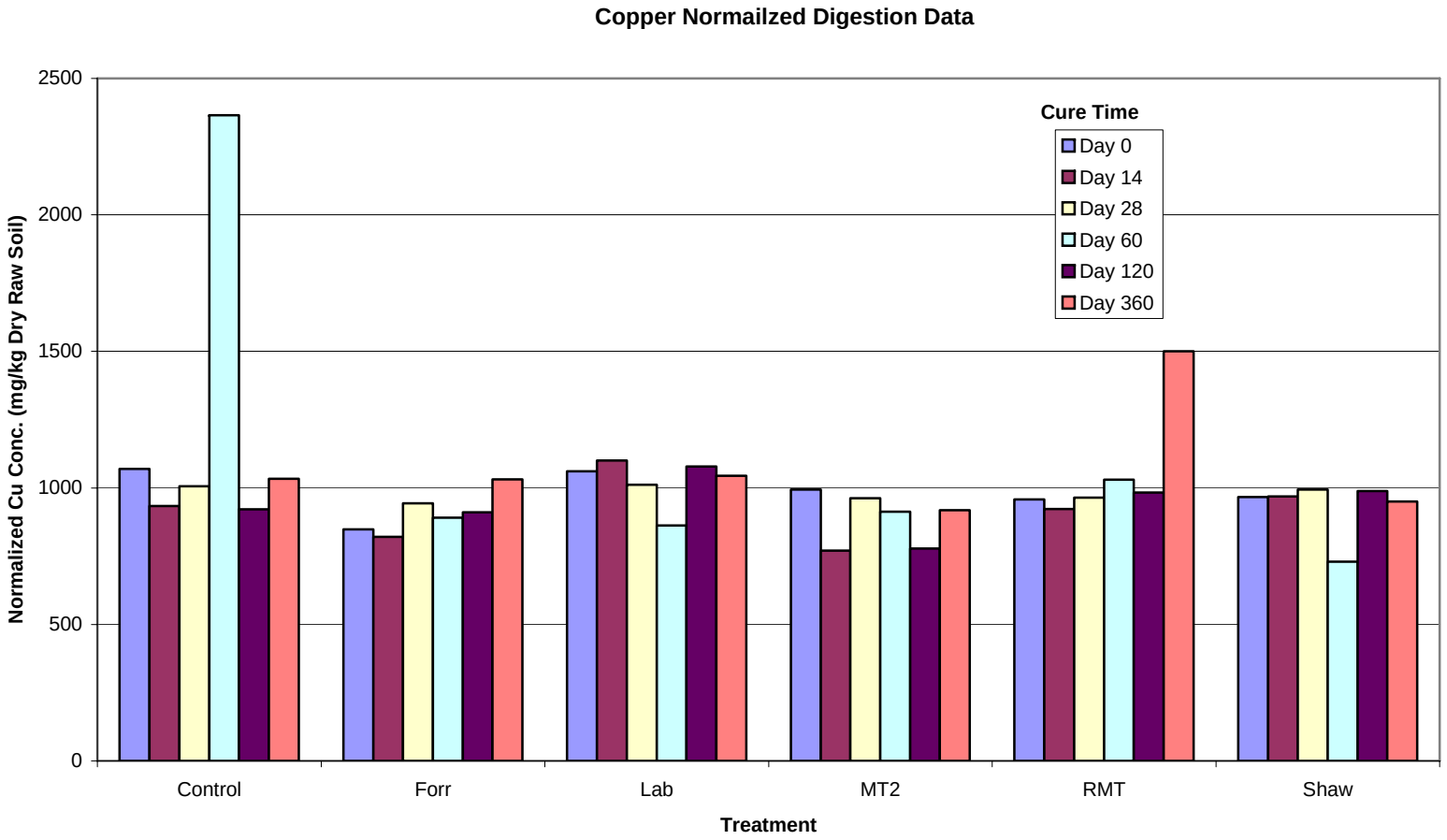

Figure D-3. Normalized digestion data for copper.

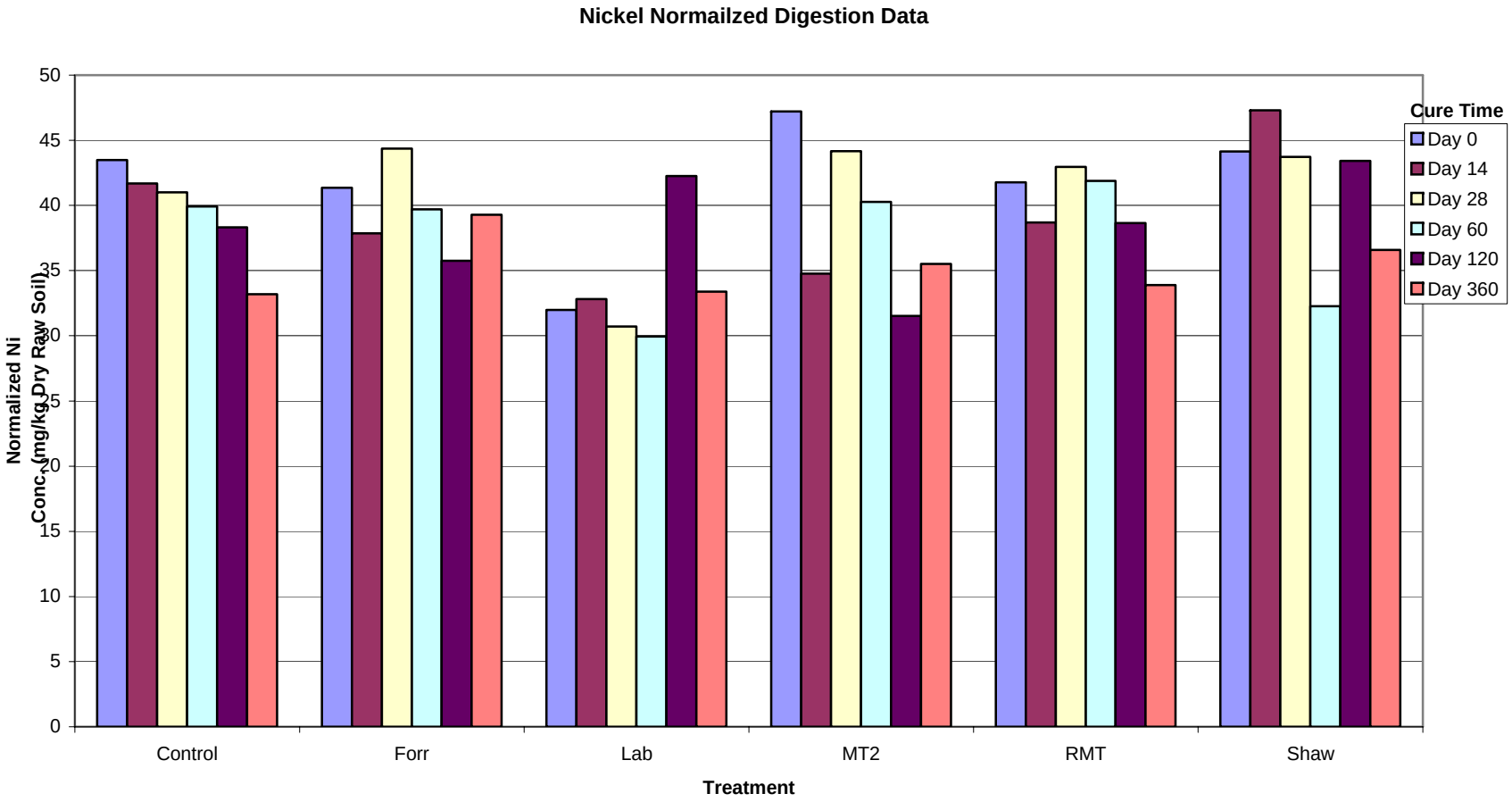

Figure D-4. Normalized digestion data for nickel.

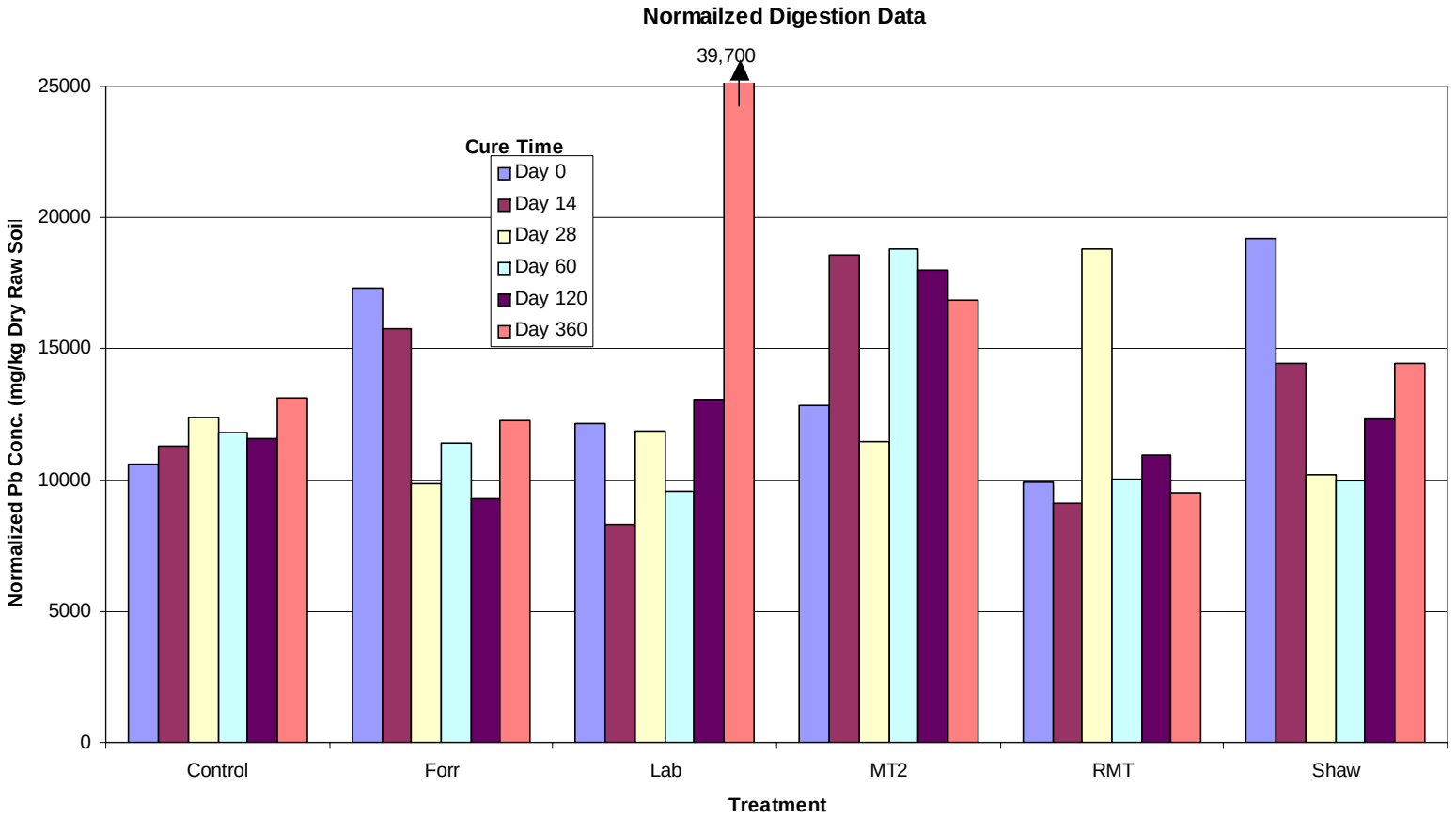

Figure D-5. Normalized digestion data for lead.

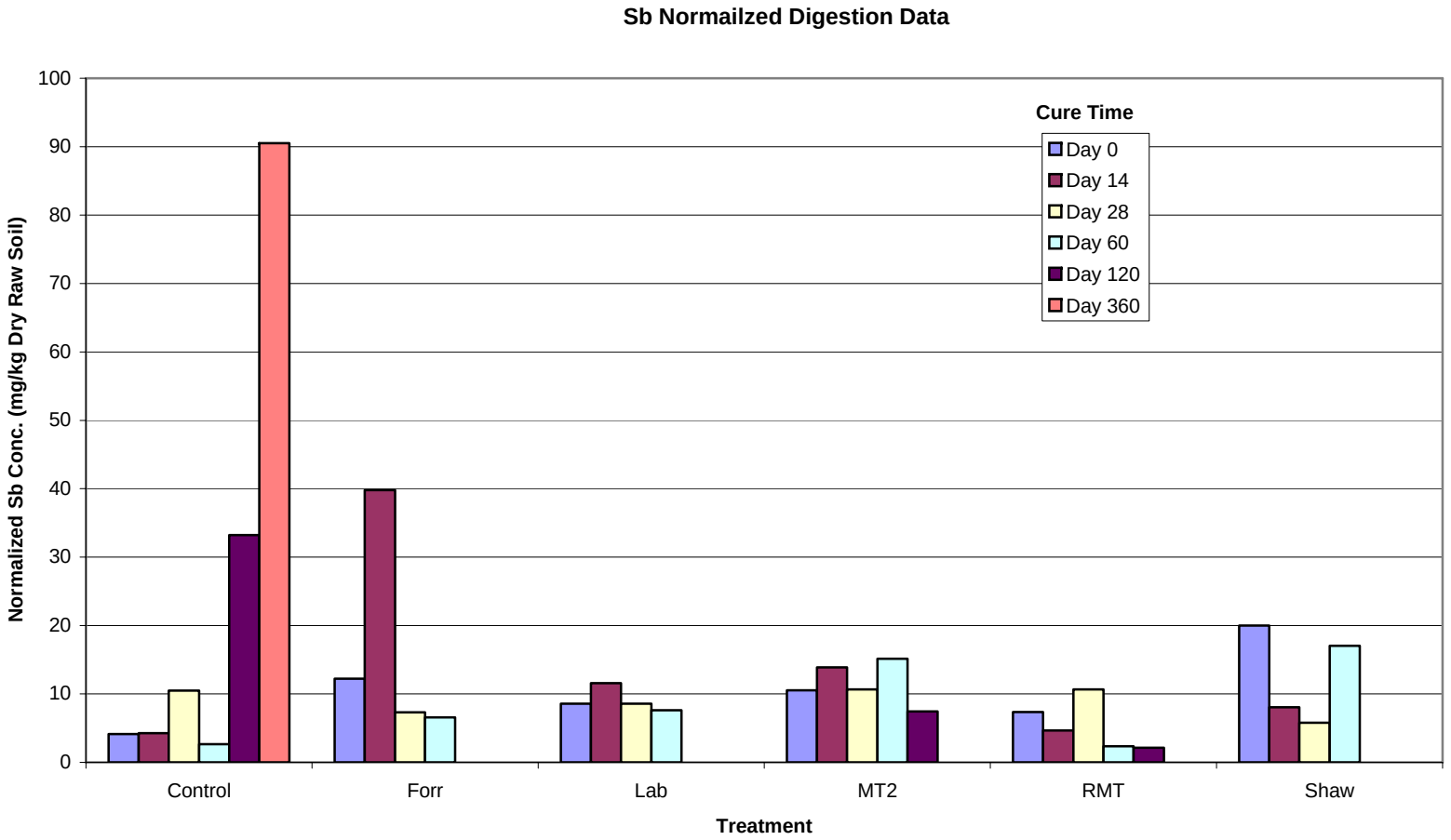

Figure D-6. Normalized digestion data for antimony.

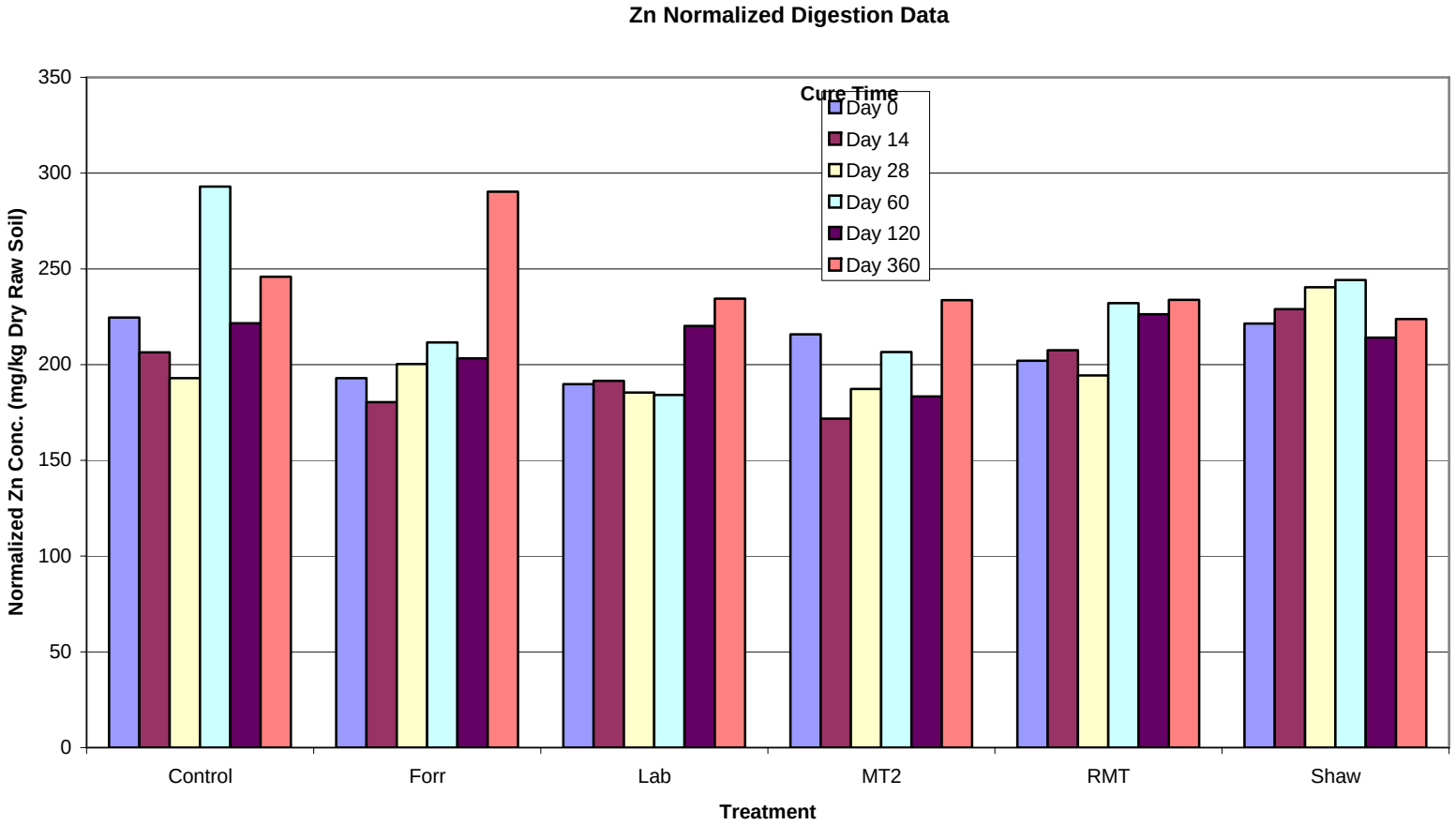

Figure D-7. Normalized digestion data for zinc.

APPENDIX E. DI LEACH STUDY DATA BAR GRAPHS

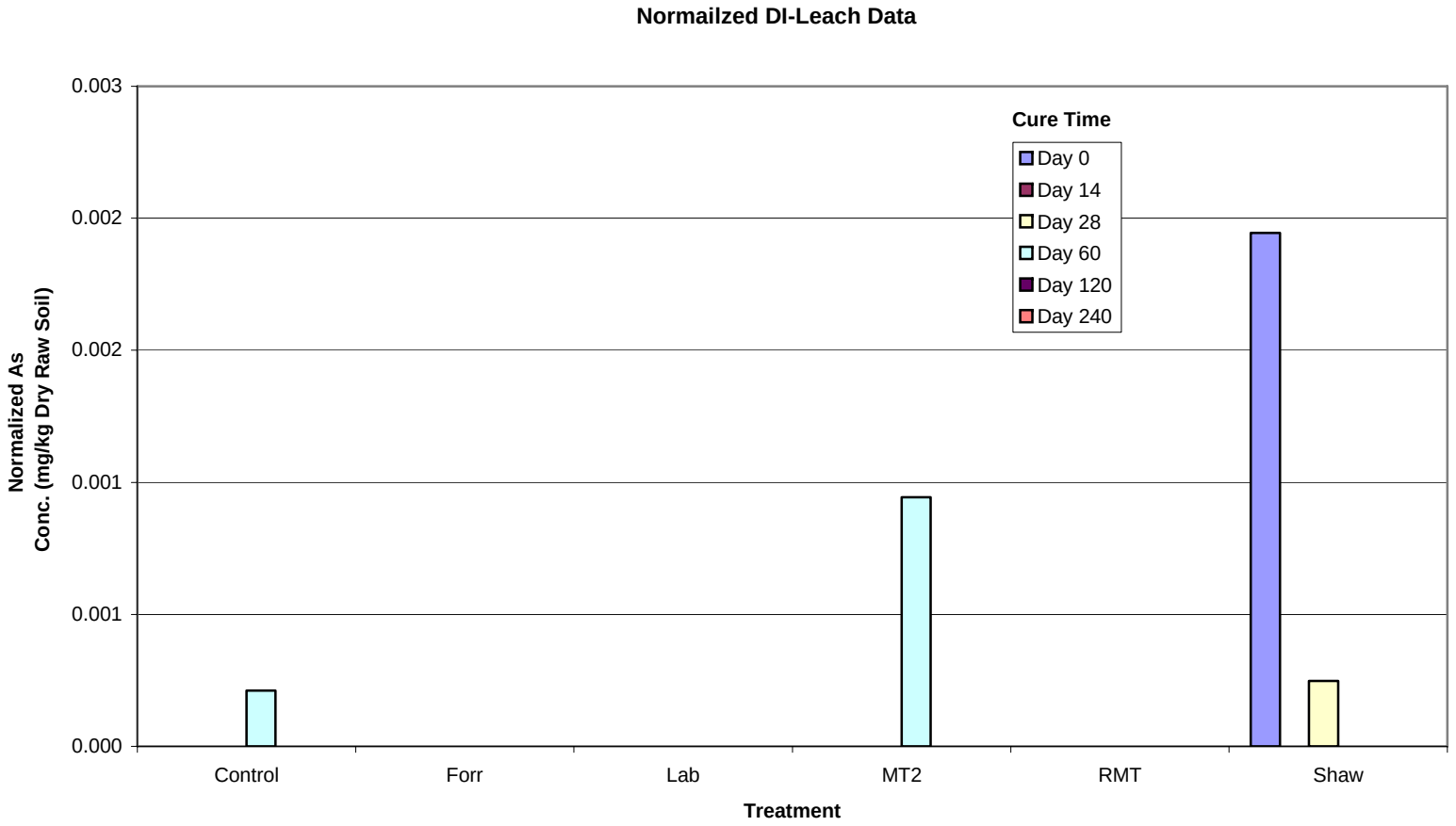

Figure E-1. Normalized DI data for arsenic.

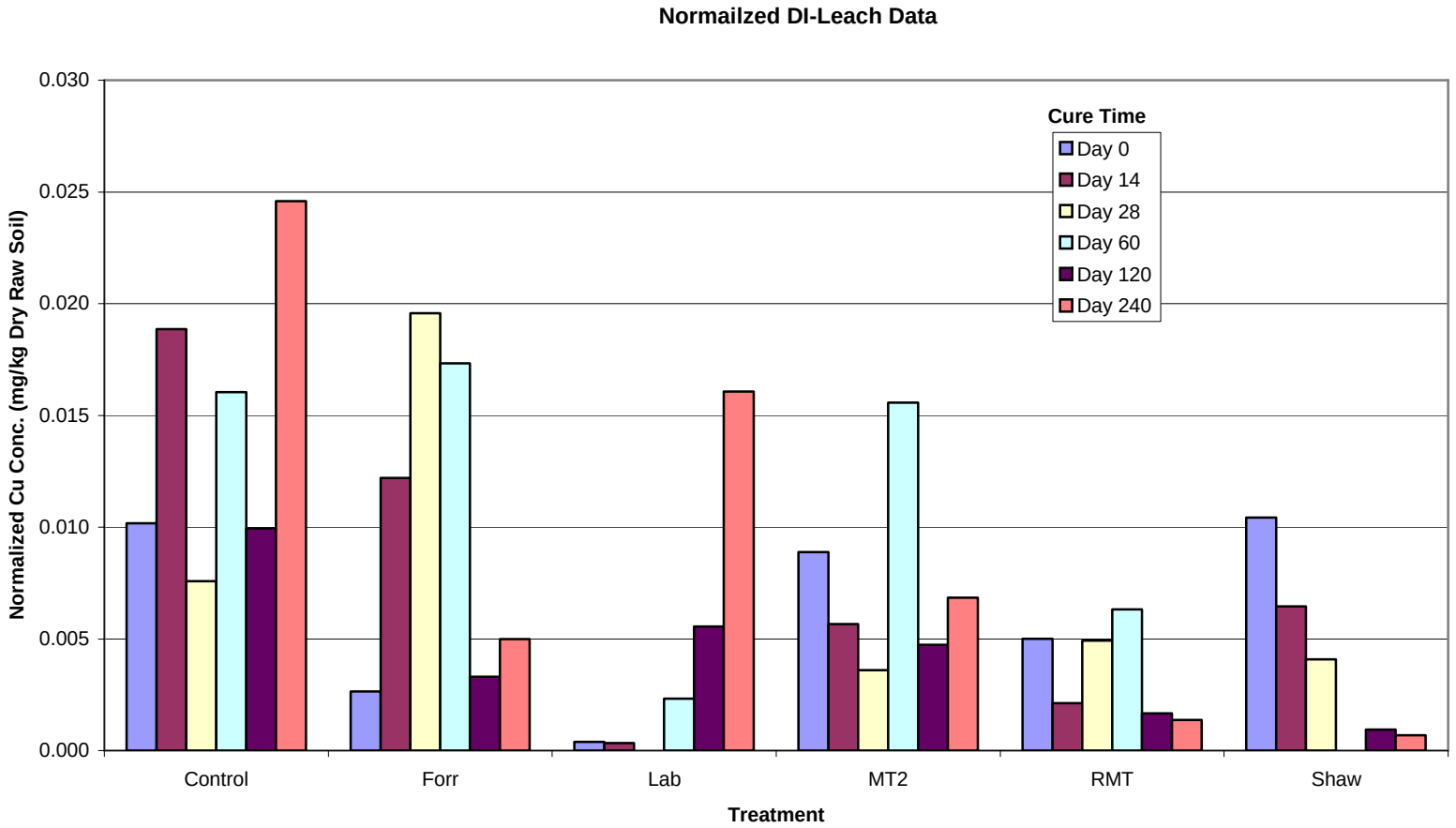

Figure E-2. Normalized DI data for copper.

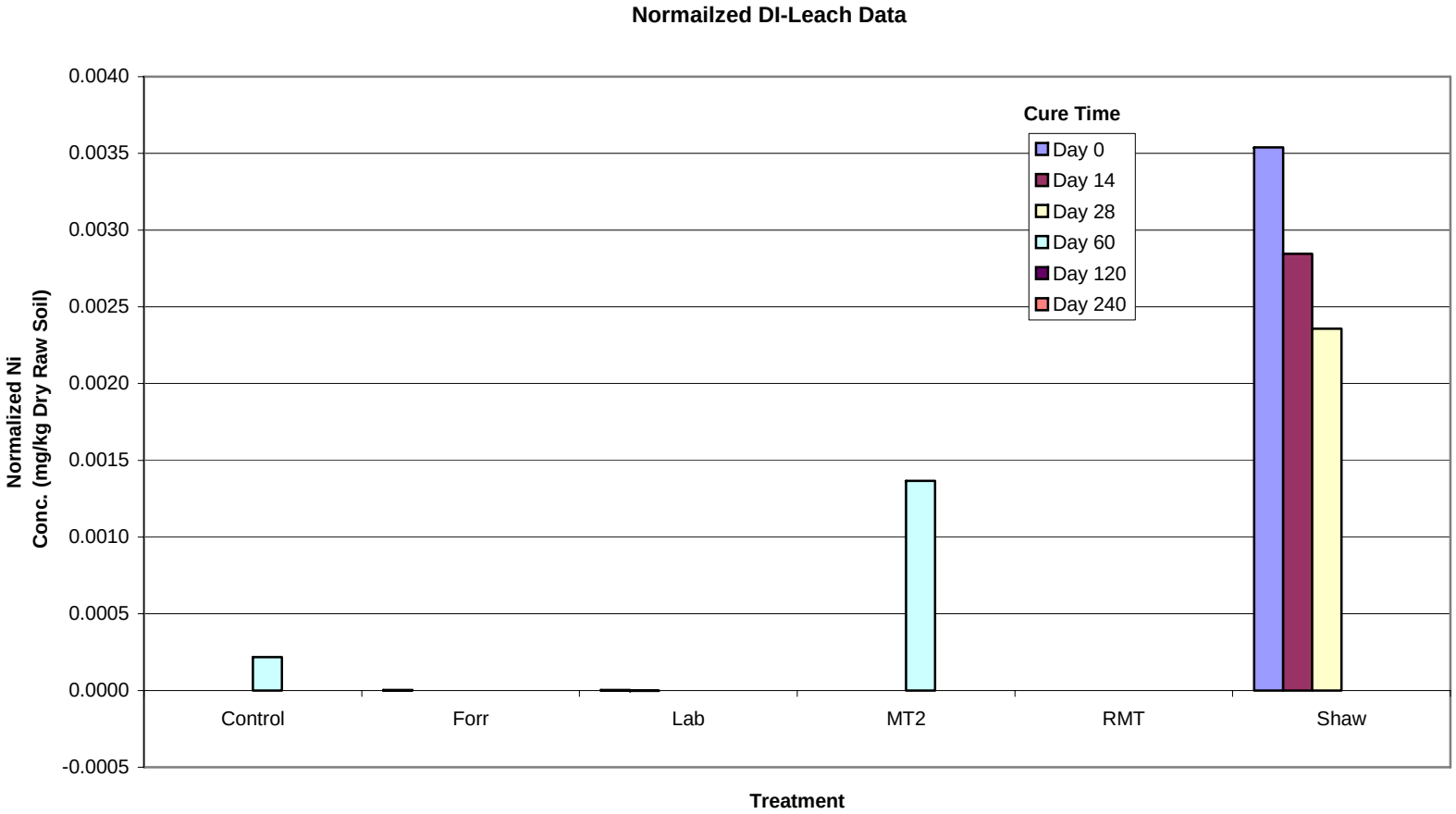

Figure E-3. Normalized DI data for nickel.

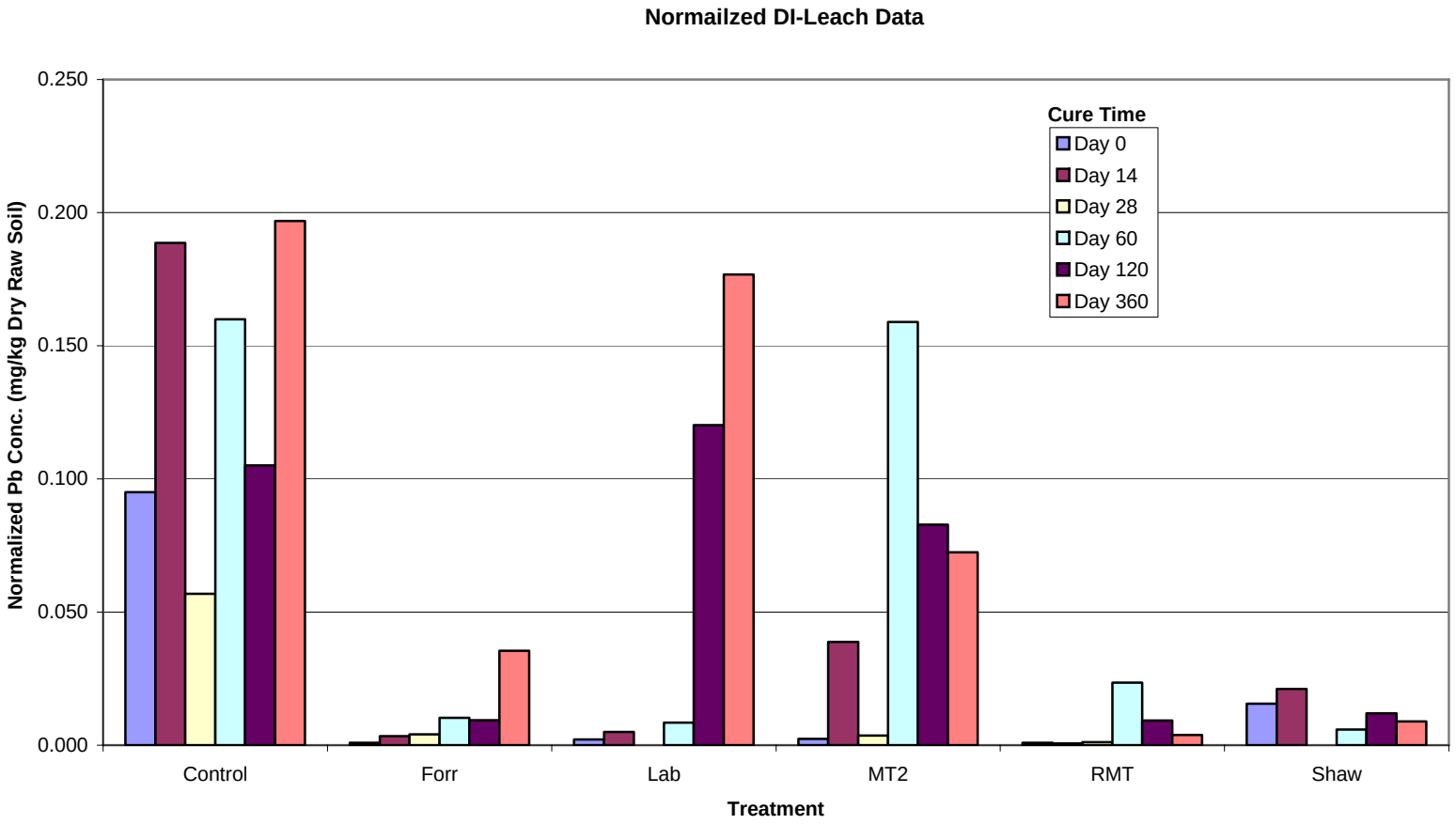

Figure E-4. Normalized DI data for lead.

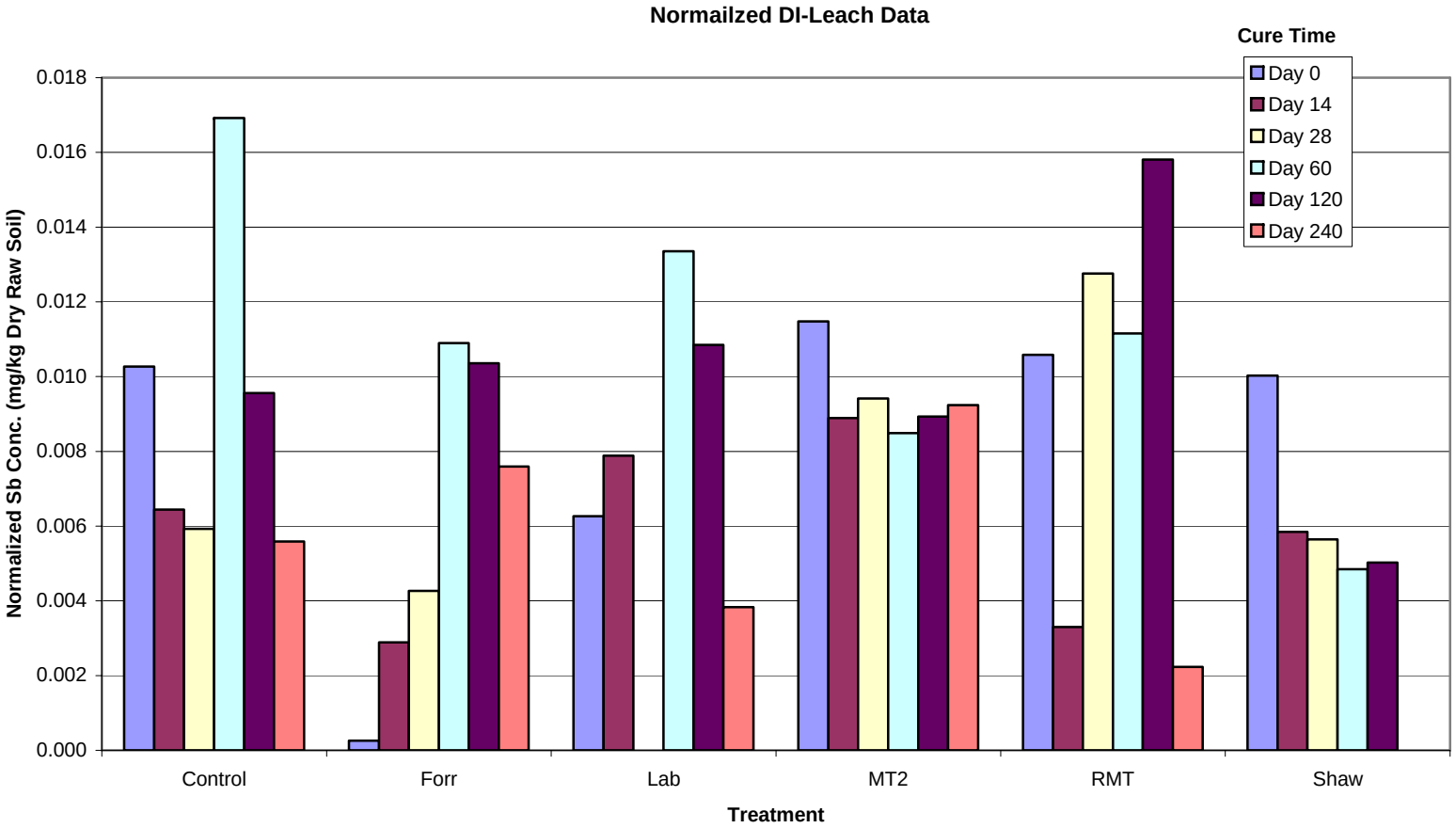

Figure E-5. Normalized DI data for antimony.

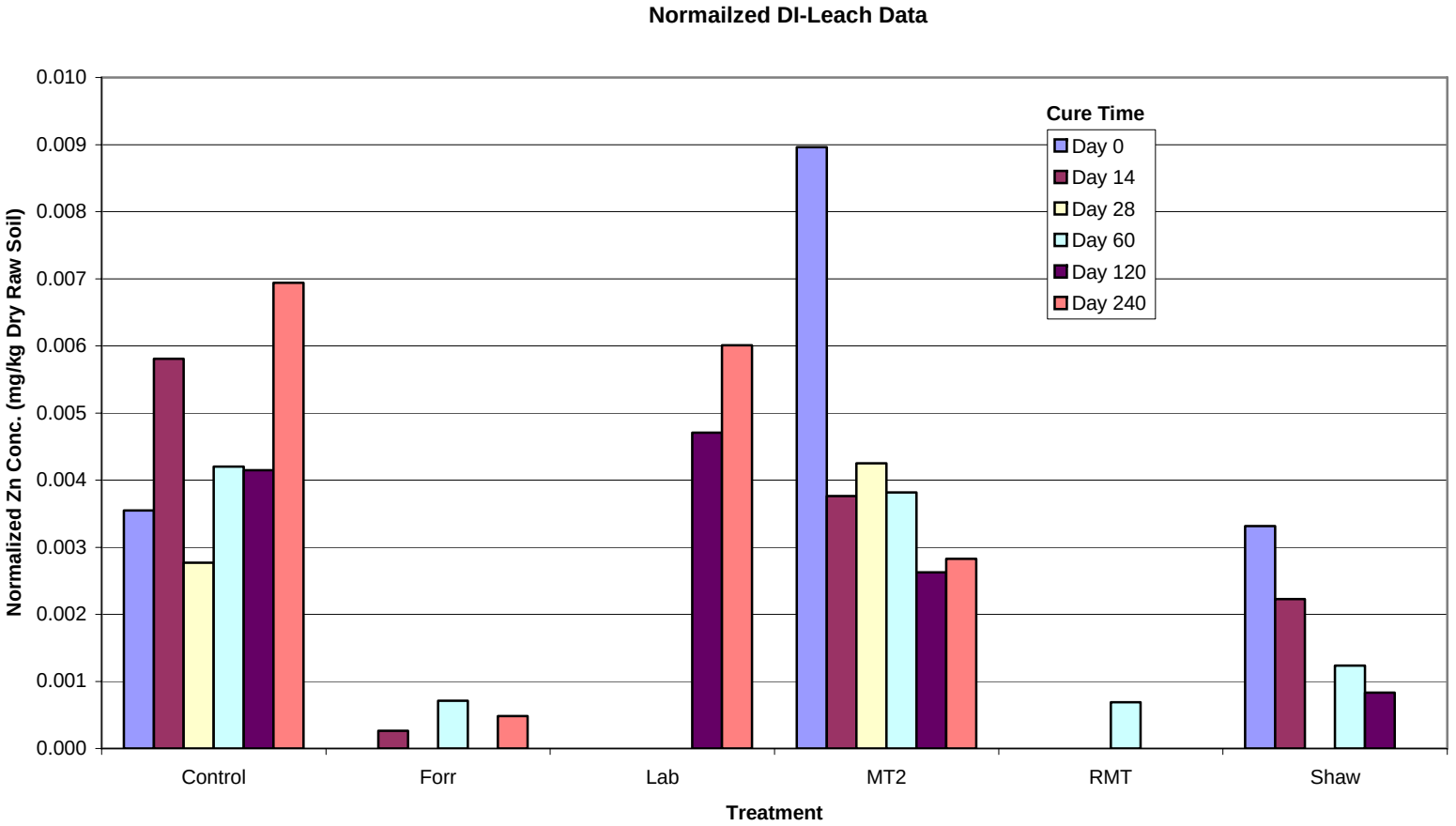

Figure E-6. Normalized DI data for zinc.

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APPENDIX F. TCLP STUDY DATA BAR GRAPHS

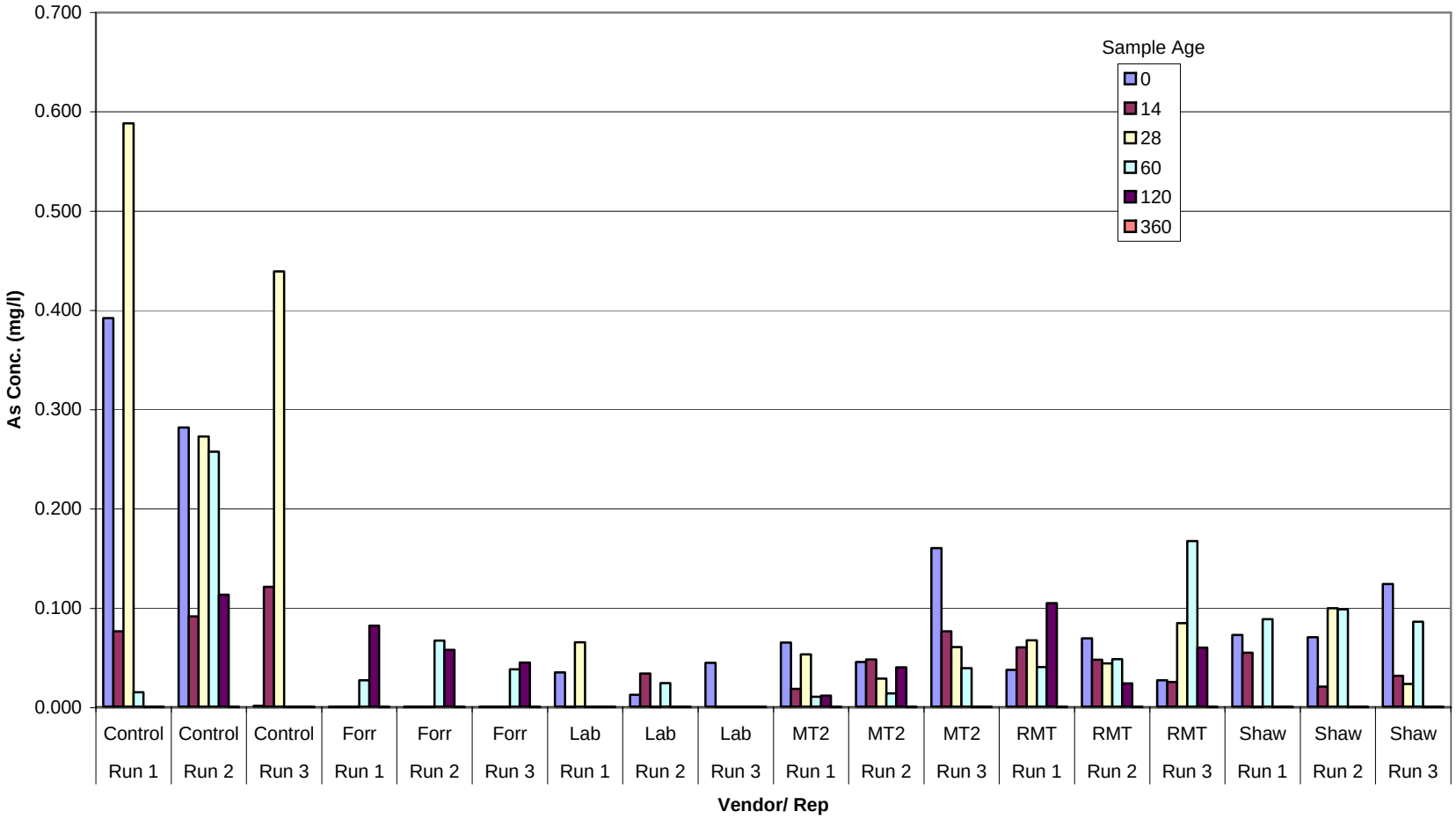

Figure F-1. TCLP data for arsenic.

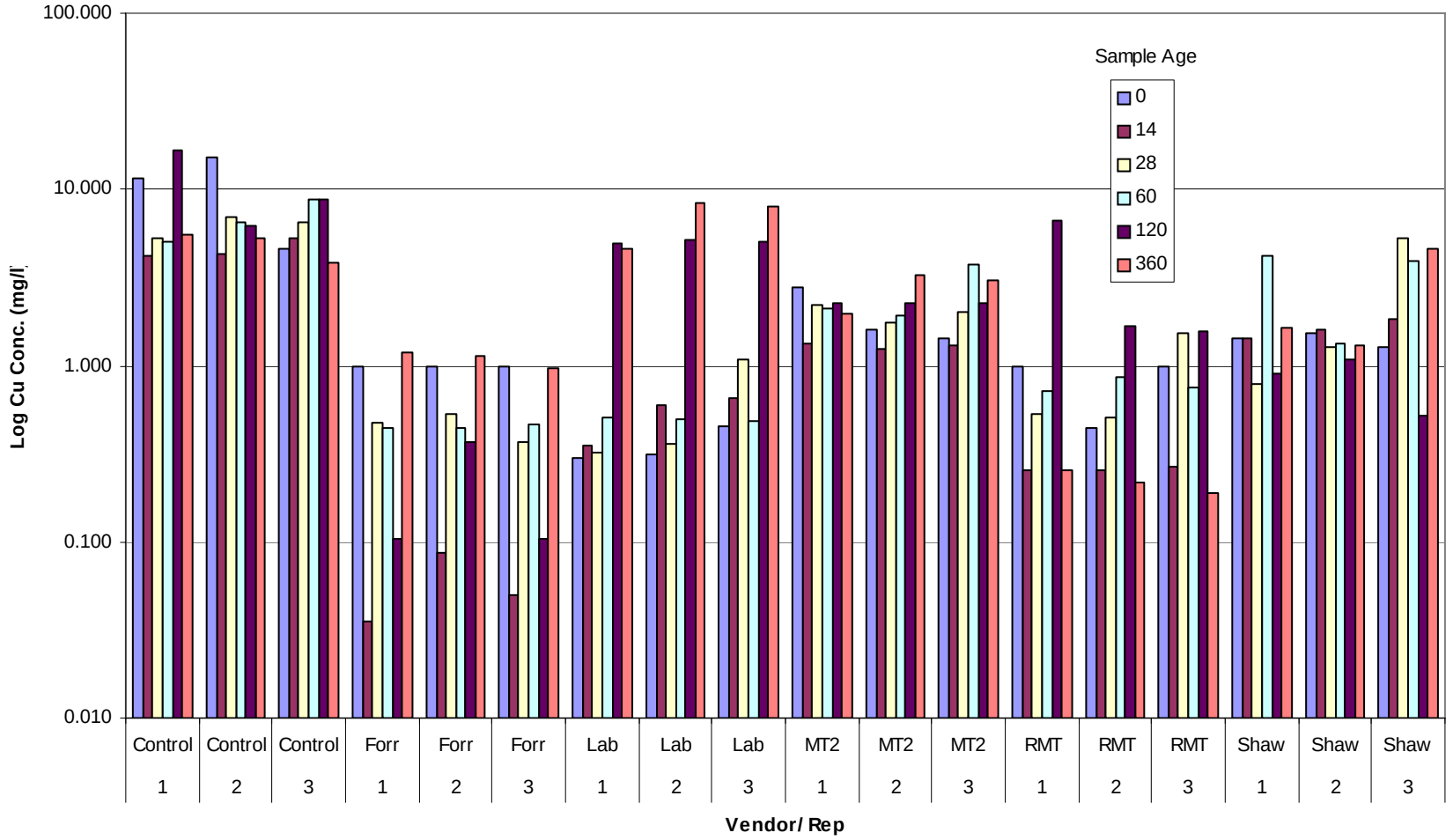

Figure F-2. TCLP data for copper (log concentration in mg/L).

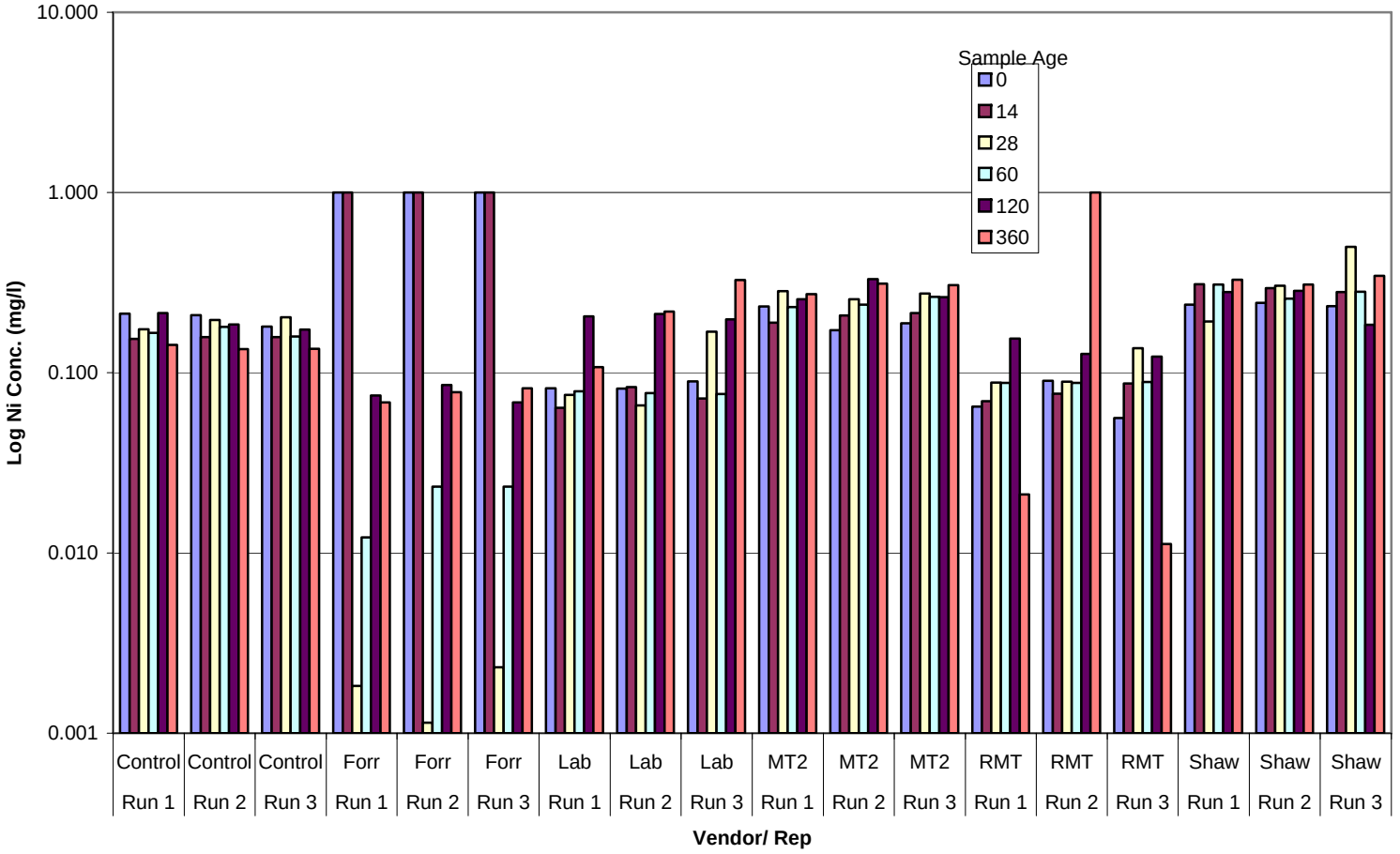

Figure F-3. TCLP data for nickel (log concentration in mg/L).

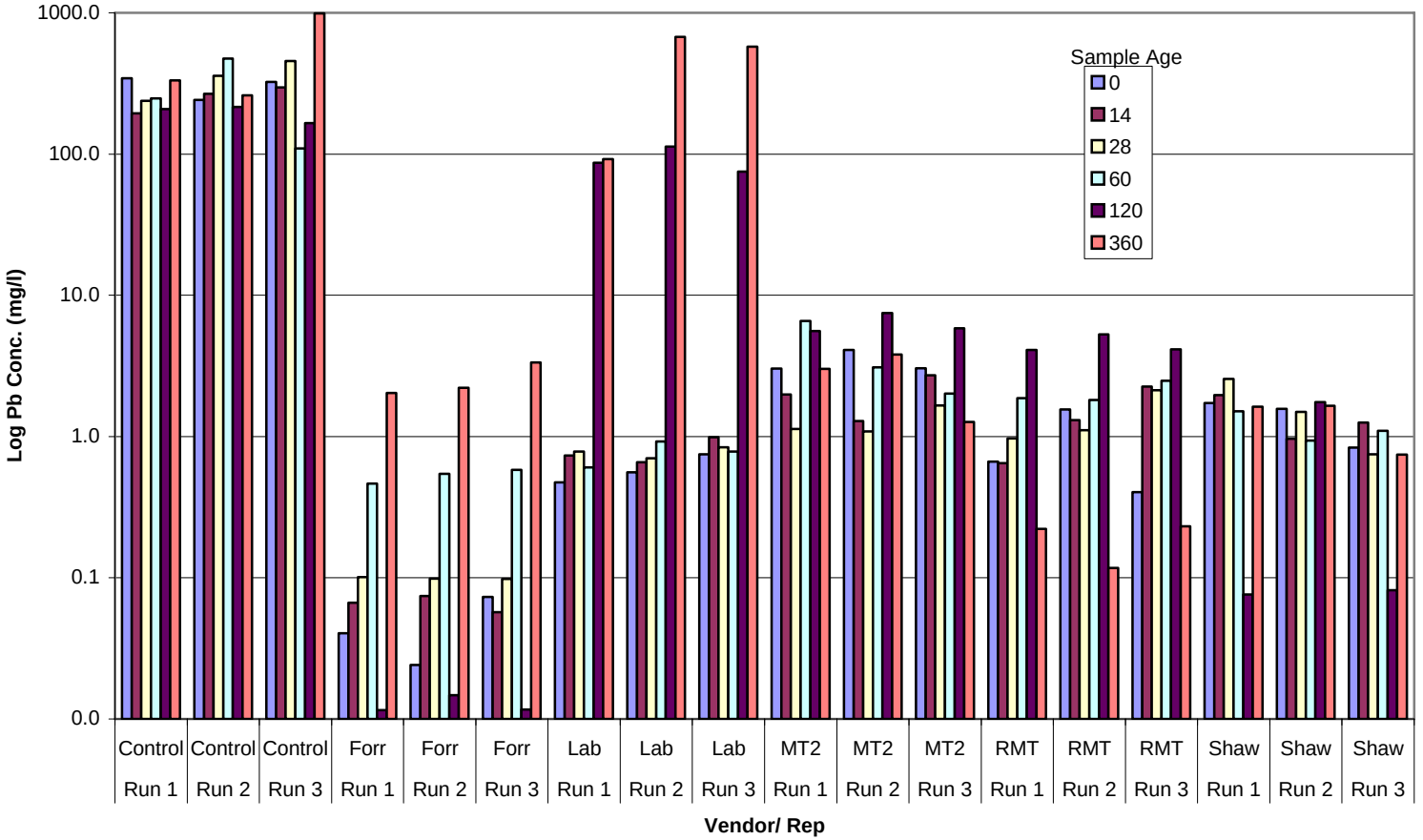

Figure F-4. TCLP data for lead (log concentration in mg/L).

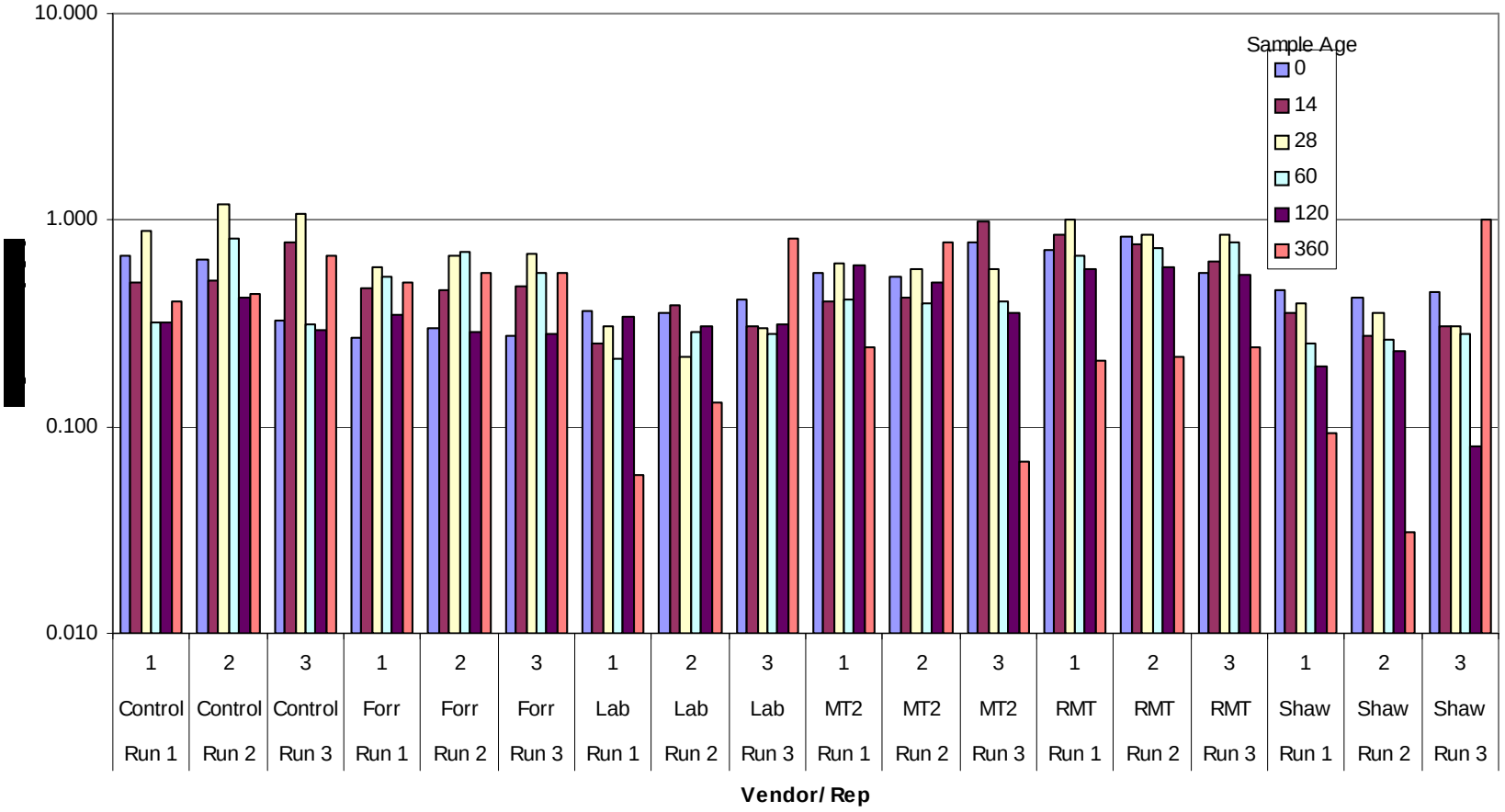

Figure F-5. TCLP data for antimony (log concentration in mg/L).

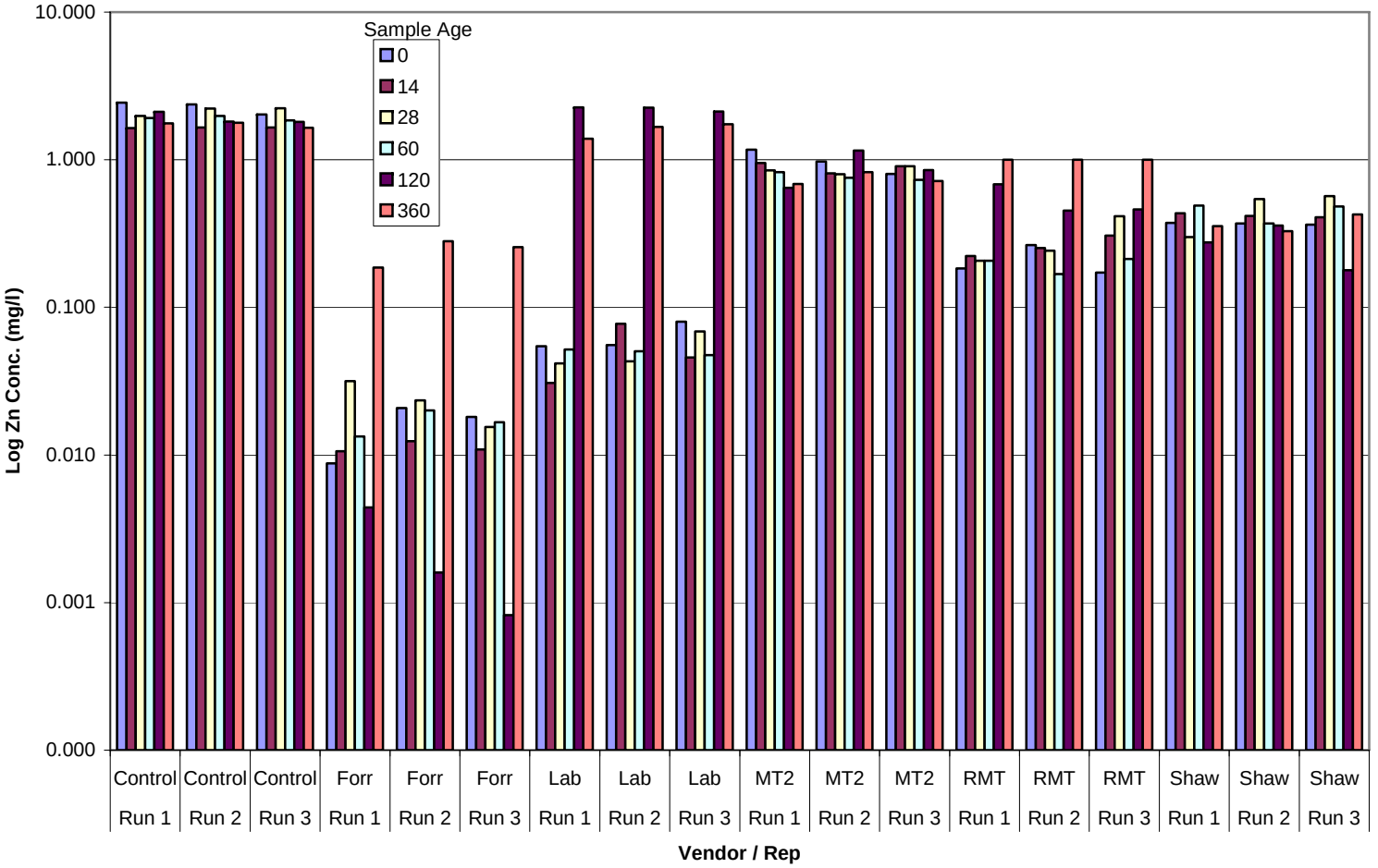

Figure F-6. TCLP data for zinc (log concentration in mg/L).

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APPENDIX G. SPLP STUDY DATA BAR GRAPHS

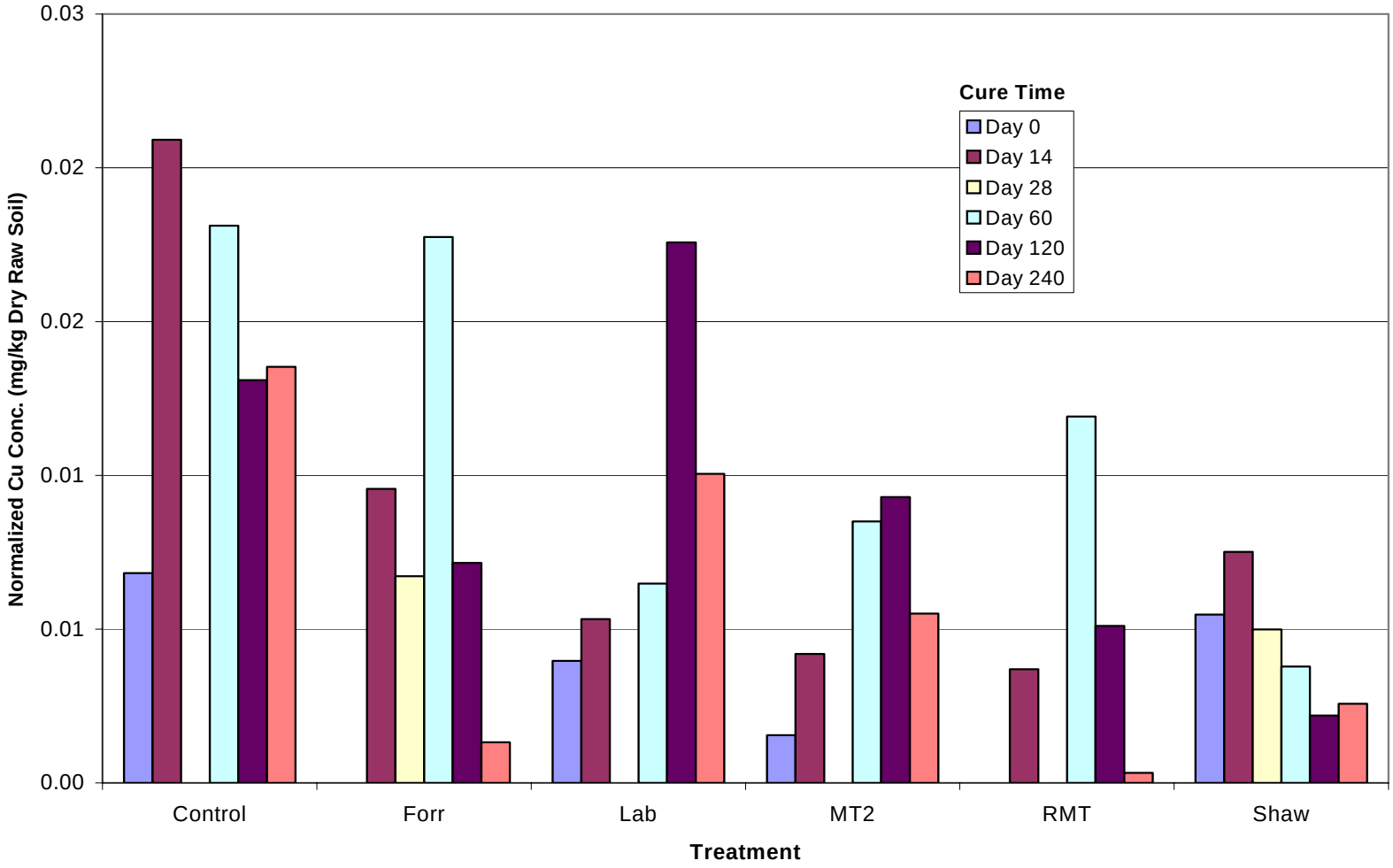

Figure G-1. Normalized SPLP data for copper.

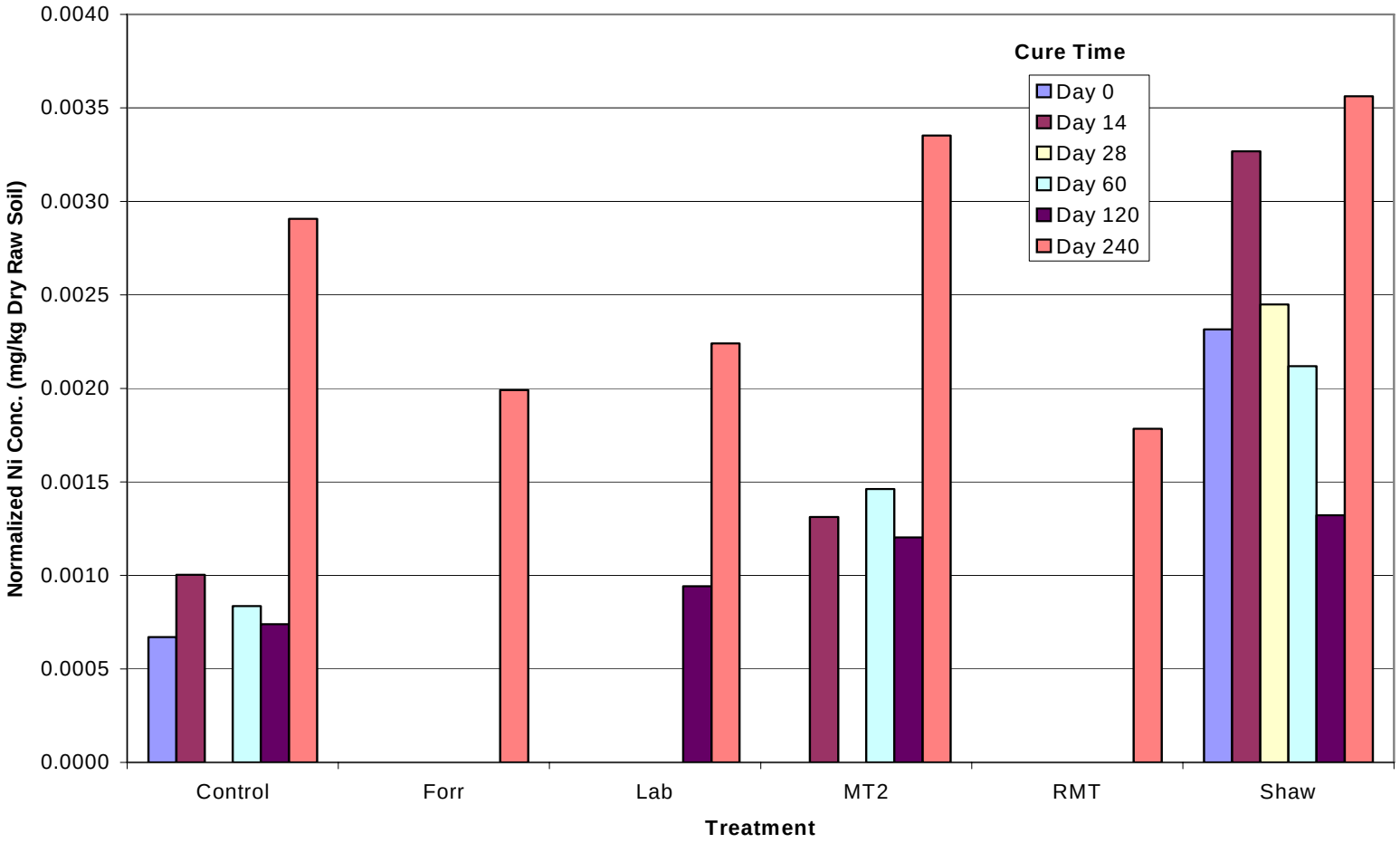

Figure G-2. Normalized SPLP data for nickel.

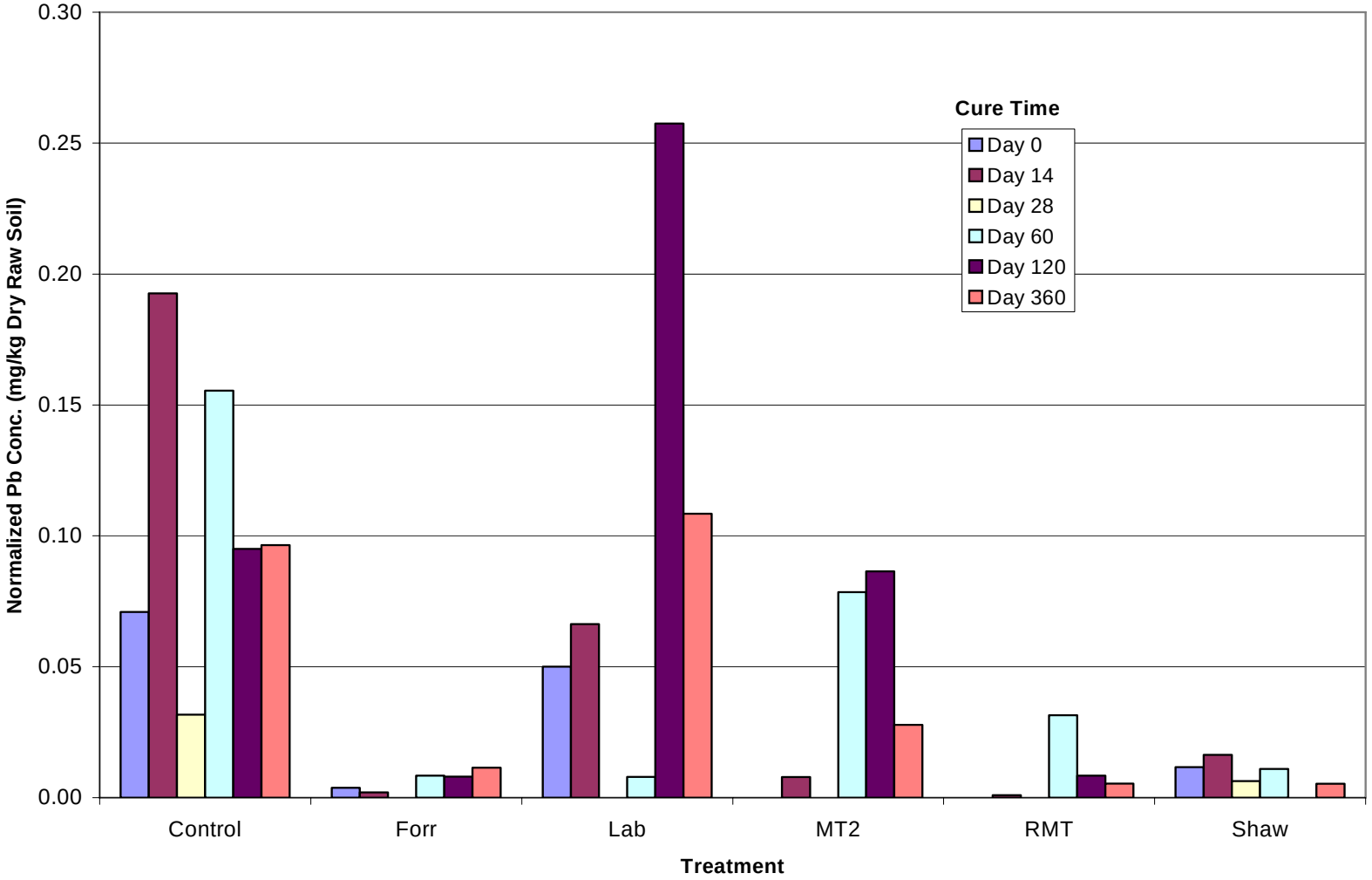

Figure G-3. Normalized SPLP data for lead.

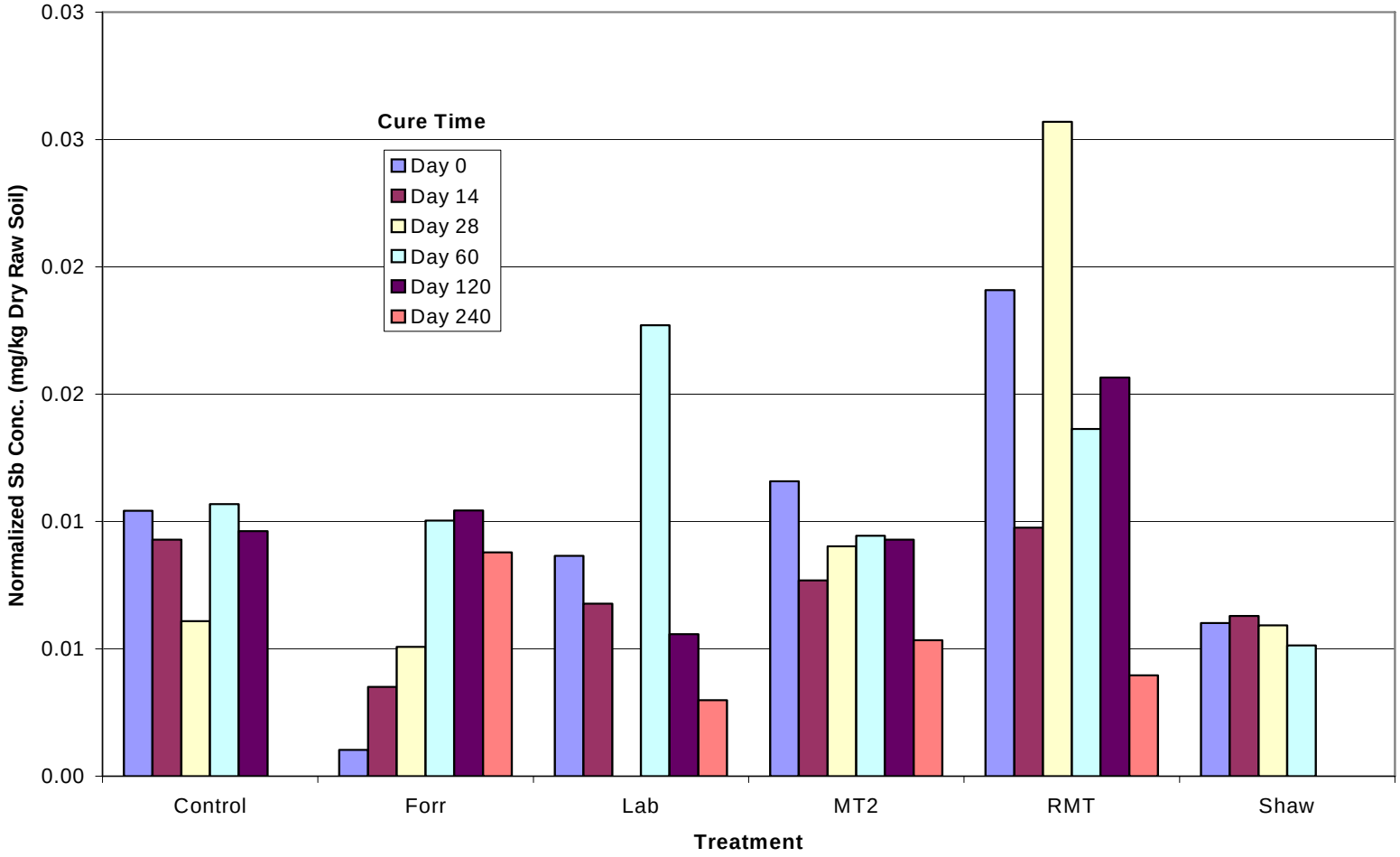

Figure G-4. Normalized SPLP data for antimony.

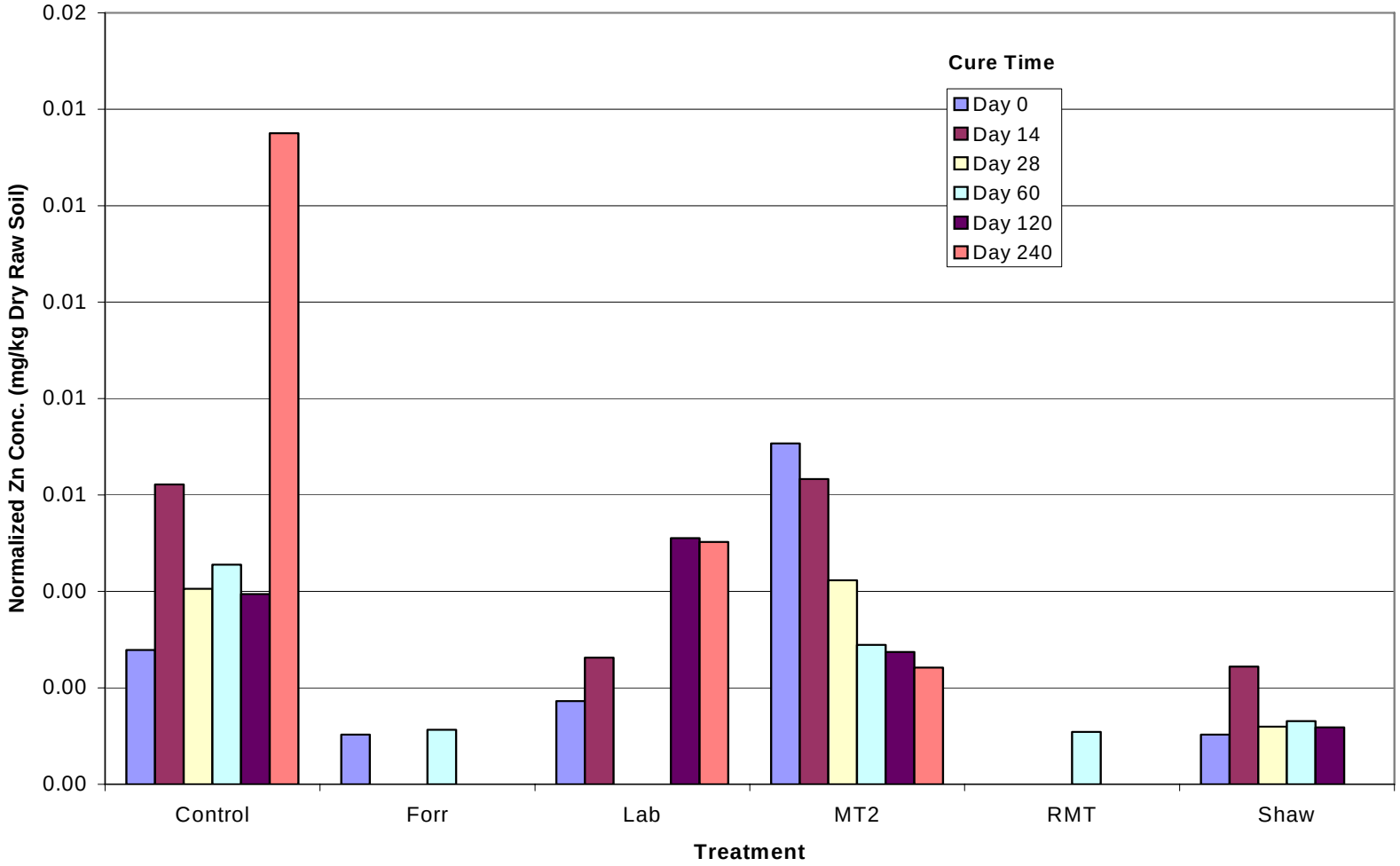

Figure G-5. Normalized SPLP data for zinc.

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